



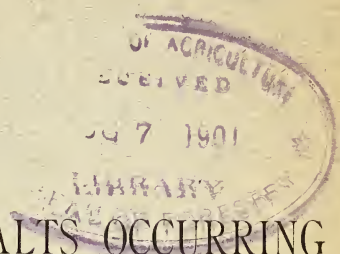
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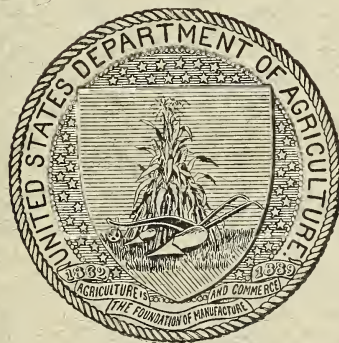
U. S. DEPARTMENT OF AGRICULTURE,
DIVISION OF SOILS.
MILTON WHITNEY, Chief.



SOLUTION STUDIES OF SALTS OCCURRING
IN ALKALI SOILS.

BY

FRANK K. CAMERON, LYMAN J. BRIGGS,
AND ATHERTON SEIDELL.



WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1901.

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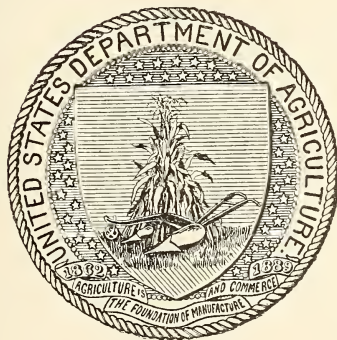
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LETTER OF TRANSMITTAL

U. S. DEPARTMENT OF AGRICULTURE,

DIVISION OF SOILS,

Washington, D. C., June 1, 1901.

SIR: I have the honor to transmit herewith a technical paper on Solution Studies of Salts Occuring in Alkali Soils, giving the results of certain investigations carried on in the laboratories of this Division which have an important economic bearing on the alkali problem of the arid lands of the West, and, in general, on the nature and composition of soils.

In accordance with the usual practice in such matters, this manuscript has been submitted to the Chief Chemist of the Department for approval of the chemical methods involved.

Respectfully,

MILTON WHITNEY,

Chief of Division.

HON. JAMES WILSON,

Secretary of Agriculture.

PREFACE.

The investigations described in this Bulletin have been made within the past year (in the laboratories of soil chemistry and soil physics of the Division of Soils) for the purpose of elucidating problems or difficulties encountered by the field parties in their work, for which adequate published data were not available.

In many cases the investigations have been carried beyond the point necessary to answer the specific questions for which they were undertaken. This has seemed advisable, as unlooked for questions have arisen during the progress of the work, and a clear understanding of the problems could be obtained only by a more complete study. A just criticism would be that for the most complete scientific value the investigations should have been carried out more completely and in further detail. This has been clearly recognized, but the exigencies of the public service and the limited time available for this work have not permitted the more exhaustive examination of the subjects. The work here recorded is rather to be regarded as preliminary investigations to open the field for study. Moreover, these studies have been made essential integral parts of a systematic line of investigation on the properties of soil solutions which the Division has undertaken.

The importance of the general investigation has been dwelt upon at length in recent publications of this Division, and it will be necessary only to recall the fact that a comprehensive knowledge of the nature and functions of soil solutions is absolutely essential to a rational study of such practical problems as the relation of crops to soils, or to soil fertilizing, to illustrate the economic importance of any investigation which can throw light upon the subject.

This Bulletin is essentially a technical paper, and it is not the purpose to consider specific practical applications of the investigations described, although some of them are referred to for the purpose of illustration. It would seem that the practical application can best be considered in the reports of the field parties, when the problems themselves are under discussion, but some general applications of the work may with advantage be pointed out here.

The investigations described in this Bulletin are more especially concerned with problems presented by "alkali" lands in the arid regions of this country. There is a characteristic difference between the studies of soils in humid and arid regions. In the soil solutions of humid regions there are small amounts of constituents, derived

from the slightly soluble soil components, which make the solution a culture medium for plant growth. These mineral plant nutrients, both as to their absolute amount and relative proportions, are of the first importance in the study of these soils. In the soils of arid regions these necessary plant nutrients are also present, and usually in sufficient amounts; but generally there are also present considerable quantities of readily soluble mineral salts, which may be, and often are, a serious detriment to plant growth, and it is these excessive amounts of soluble salts which command more immediate attention. Nevertheless, the chemical and physical phenomena presented by soils both from the arid and humid regions are essentially the same.

From their nature soils from the humid areas present analytical and mechanical obstacles which make the study of the ground solutions in them exceedingly difficult. On the other hand, these difficulties are much less with soils from the arid regions. It is natural and proper, therefore, that the study of the soils of the arid regions should develop more rapidly and precede the study of the soils of the humid regions, and that the general features of the problems involved should be mastered in the former study, before applying the methods there worked out to the latter study. The attempt is now being made in the laboratories of this Division to study certain soils from humid areas according to the ideas which have been developed in the investigation of alkali soils, and it is believed with a gratifying promise of success.

The presence of soluble carbonates or, more probably, hydrogen carbonates is to be expected in all soils. In humid soils they are present only in very small amounts, and their characteristic properties are generally more or less masked by the presence of an excess of dissolved carbon dioxide or carbonic acid in the soil solutions. The soil atmosphere has been shown to be unusually rich in carbon dioxide—certainly as compared with the atmosphere above the soil—and this is true even in well-drained and well-aerated soils, so that considerable amounts of dissolved carbon dioxide are to be expected in the soil solution, since the solubility of the substance is dependent upon the partial pressure it exerts in the gas phase or atmosphere in contact with the solution.

In arid regions the amounts of soluble normal carbonates and hydrogen carbonates in the soil are occasionally quite large. It has been suspected for some time that the normal carbonates and hydrogen carbonates play quite a different rôle in their relations to crop culture, as well as to the other soil components. These suspicions have been confirmed by laboratory investigations and field observations. It has become an economic necessity, therefore, to distinguish between the normal carbonates and the hydrogen carbonates present in the soil, in irrigation and drainage waters.

The relative amounts in which the normal carbonates and hydrogen

carbonates will be present in a solution are naturally dependent upon one another and upon certain other factors, including temperature, composition of the atmosphere in contact with the solution, etc. The carbonates and hydrogen carbonates of the alkali metals and alkali earth metals have many features in common when in aqueous solution, but they also present well-marked differences.

While these facts were more or less clearly realized, our knowledge of them and of the mutual relations between them was too indefinite and uncertain to explain satisfactorily, even in a qualitative way, the phenomena observed in the field work. Even less was this knowledge sufficient to enable one to predict the changes in the soil solutions with changing conditions. That such knowledge would have an immense importance in an intelligent use and control of irrigating waters in lands containing soluble carbonates is self-evident. Some idea of the probable modifications which will occur in such soils can now be formed on the basis of the investigation here recorded on the equilibrium between normal carbonates and hydrogen carbonates in aqueous solutions. The effect of drainage upon such lands can now be predicted with some confidence. Incidentally, much information of importance in studying geological as well as soil problems has been brought out. It seems certain, moreover, as Dr. Cameron points out, that the data presented may find a large usefulness in certain technical processes involving the manufacture or employment of alkali carbonates.

It has been pretty definitely shown that the predominating chemical feature of most, if not all, alkali regions is the interaction of certain soluble salts in aqueous solutions upon less soluble salts—notably gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and calcium carbonate (CaCO_3). While certain general features of such systems could be recognized on the basis of the electrolytic dissociation hypothesis, practically no precise knowledge was available. It was essential for a correct understanding of the phenomena that they should be studied in the laboratory under conditions which are simpler and more readily controlled than those that usually obtain in the field.

The solubility curves established in the investigations here recorded have brought out several facts which were quite unforeseen and which have a great importance in the study and control of alkali soils. The time is surely approaching, if it has not already arrived, when the agriculturist in the arid regions will demand further assistance than the information that his soils need irrigation or under-drainage or both. He has a right to expect expert opinion as to the probable specific effects of such treatment on his soils. The importance of calcium in the soil solutions in enabling crops to withstand excessive amounts of other salts is but one of the many factors which is becoming recognized. The relative proportions in which the different base-ions and acid-ions occur in the soil solutions in relation

to their adaptability for various crops—and will occur after cultivation and irrigation—is becoming more evidently important as the study of soil solutions proceeds.

The transportation of gypsum and lime carbonate in the soil and their reprecipitation, sometimes in porous layers and sometimes as a detrimental hardpan, is of great economic importance. The use of gypsum or land plaster on soils containing carbonates has long been known, but its rationale has needed clearing up. Incidentally, it has been pretty clearly indicated that the application of calcium sulphate to other classes of soils may have economic results of considerable value.

The solubility determinations described in this Bulletin are fundamental and necessary to a successful investigation of such questions. Not the least of their uses is in pointing out a line of attack upon the exceedingly difficult and perplexing problem of the use of mineral fertilizers upon the soils of humid regions. Their importance in certain geological problems needs no further comment.

Analytical investigations of alkali soils have been numerous, and nearly as numerous have been the procedures and methods employed. This state of affairs presents the very unfortunate feature that the work of various investigators, no matter how valuable it may be in itself, can not be intelligently used in comparative studies. Considerable attention has been given to this subject, and a method of procedure has been developed in the laboratory of this Division which it is believed will give more rational results than any other yet proposed, and which in its salient features, if not in its entirety, must ultimately be adopted by investigators in this field by general convention. It presents some arbitrary features, necessitated by the limitations of our knowledge, but it is believed to be as free from objections on this score as is now possible. A detailed description of this analytical scheme has therefore been prepared for this Bulletin and also an account of the development of the method now used in the work of this Division for the field estimation of carbonates, bicarbonates, and chlorides—with certain extensions and modifications for particular conditions.

MILTON WHITNEY.

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SOLUTION STUDIES OF SALTS OCCURRING IN ALKALI SOILS.

EQUILIBRIUM BETWEEN CARBONATES AND BICARBONATES IN AQUEOUS SOLUTION.

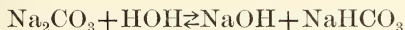
By FRANK K. CAMERON and LYMAN J. BRIGGS.

STATEMENT OF THE PROBLEM.

If an aqueous solution of sodium carbonate be allowed to come to equilibrium in contact with the air, there is always formed a greater or less amount of the hydrogen carbonate, more generally known as bicarbonate.

The system is then quite complex; for, in addition to the normal carbonate and the hydrogen carbonate, there is present also sodium hydroxide from the hydrolysis of the salt, dissolved carbon dioxide, possibly carbonic acid, and the various electrolytic dissociation products. If the sodium hydrogen carbonate be considered alone, the concentration of the solution with respect to this salt will be dependent upon several factors.

(1) It is obviously dependent on the amount of normal sodium carbonate present, for it is one of the products resulting from the hydrolysis of that substance, as is indicated by the scheme

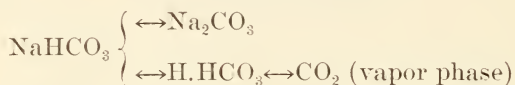


(2) It will depend obviously upon the temperature, for the amount of hydrolysis of the normal carbonate is dependent upon the temperature. Further, the amount of carbon dioxide and, in consequence, the carbonic acid in the solution is a function of the temperature.

(3) It will depend upon the partial pressure of carbon dioxide in the vapor phase in contact with the solution; that is to say, upon the amount of carbon dioxide per unit volume in the atmosphere above the solution. Upon this partial pressure in the vapor phase will depend the amount of the carbon dioxide dissolved in the solution and obviously the amount of the normal carbonate which will be converted by it to the hydrogen carbonate. Further, sodium hydrogen carbonate, being a salt composed of a strong base in contact with a weak acid, would be hydrolyzed unless the hydrolysis be forced back by an

excess of the weak acid in solution. Walker and Cormack¹ have shown that the ions resulting from the solution of carbon dioxide in water are mainly H^+ and HCO_3^- , and to a very much less extent the ion CO_3^{--} . More recently Bodlander² has shown that the dissociation, with formation of HCO_3^- ions is about twenty thousand times as great as with the formation of CO_3^{--} ions.

Supposing the temperature to remain constant, and omitting the formal statement of the details, these facts might be schematically arranged thus:



where the double-headed arrow is taken to mean "is dependent upon." This schematic arrangement indicates that if some effective means were devised by which the carbon dioxide could be removed from the vapor phase as fast as it was formed, it would be possible to gradually remove all carbonic acid from the system and ultimately a solution of sodium hydroxide alone would remain. The experimental difficulties in the way of accomplishing this would undoubtedly be great and, as the matter does not appear to be of any practical importance, no attempt has been made to realize it.

RELATION OF THE PROBLEM TO SOIL STUDIES.

The problem of the relation of normal carbonates to the corresponding hydrogen carbonates possesses much practical interest. In the investigation of "black alkali" in the soils of arid regions it is of fundamental importance, for wherever the sodium carbonate is found the soil solution will also necessarily contain a greater or less amount of the hydrogen carbonate. Investigation in this Division has shown the latter salt (hydrogen carbonate) to be an injurious one to plant growth, but vastly less so than the normal carbonate.

A study of the recent observations of our field parties indicates that it is feasible to so modify black alkali conditions that the normal sodium carbonate can be reduced to a very low minimum by conversion to the less noxious hydrogen carbonate, this conversion depending in part upon the fact that the soil atmosphere invariably contains a relatively high percentage of carbon dioxide.³ This point will be referred to again.

While the amount of carbon dioxide in the soil atmosphere is always greater than in the air, it probably varies much with different soils

¹ Jour. Chem. Soc., 47, 5 (1900).

² Zeit. für phys. Chem., 35, 25 (1900).

³ The absorption of carbon dioxide by soils will be fully discussed by Briggs in a publication of this Division to appear at an early date.

and for any given soil under varying conditions. Our information on this point is very meager, although sporadic attempts have been made to obtain measurements in this direction from the time of Bouissangault and Lewey¹ to the present. It has seemed wise in this preliminary study, therefore, to investigate the equilibrium of the system in contact with ordinary air. It is thus possible to have a vapor phase in which the partial pressure of carbon dioxide is very constant; and, moreover, it represents the maximum condition possible in nature for the concentration with respect to the normal carbonate; that is to say, the limit beyond which no worse conditions for plant growth can exist.

DISTINCTION BETWEEN CARBONATES AND BICARBONATES.

The investigation has been made readily feasible by a method, recently devised in this Division, for the estimation of carbonates (with the hydrolized sodium hydroxide) and bicarbonates when both are in the solution simultaneously.² The method is based primarily upon the fact that carbonic acid is a stronger acid than phenolphthalein, and that the hydrolysis of the carbonate proceeds at a moderately rapid rate. It is therefore possible to continue titration with hydrogen potassium sulphate solution until there is no normal carbonate remaining in the solution. By then adding methyl orange, an acid indicator stronger than carbonic acid, the titration can be continued and the total amount of the base constituent present thus determined. From these data it is a simple matter, as will be pointed out elsewhere, to compute the amount of normal carbonate and hydrogen carbonate present.

It will be convenient to consider the system we are studying as made up of the normal carbonate and the hydrogen carbonate with this method of estimating them as the criterion between them. The normal carbonate, together with the hydrolized hydrate, will be considered under the head of normal carbonate—in contradistinction to the hydrogen carbonate which is present before the titration of the solution is commenced.

¹ Johnson (How Crops Feed, p. 139), quoting from the investigations mentioned, gives the following figures:

	CO ₂ in 10,000 parts, by weight.
Air from sandy subsoil of forest	38
Air from loamy subsoil of forest	124
Air from surface soil of forest	130
Air from surface soil of vineyard	146
Air from pasture soil	270
Air from soil rich in humus.....	543

² See paper on "Estimation of Carbonates and Bicarbonates," page 77.

EXPERIMENTS WITH SODIUM SALTS.

Solutions of sodium carbonate of various concentrations were prepared, about 200 cubic centimeters of each solution being brought into a small flask. The flasks were connected in series by a system of stoppers and tubing and were immersed in a bath the temperature of which could be closely regulated by a thermostat. Air which had previously been passed through a wash flask, containing water slightly acidulated with sulphuric acid, was then drawn continuously by means of an aspirator through the series of flasks for lengths of time varying from four days to several weeks, depending upon what was shown by experience to be necessary to bring about a state of complete equilibrium. The solutions were then removed from the bath one by one, an aliquot portion carefully measured off by running it from a burette, and the titrations made as promptly as possible with N/10 HKSO₄ solution.¹

In the accompanying tables (I, II, III, and IV) the first column gives the number of gram atoms of sodium per liter; the second column, the number of cubic centimeters of solution taken for the titration; the third and fourth columns, the number of cubic centimeters of acid solution required in the titrations; the fifth column, the percentage of the base combined as normal carbonate and its hydrolized product—the hydrate; the sixth column, the percentage of the base combined as the hydrogen carbonate.

TABLE I.—System: Na₂CO₃, NaHCO₃, and CO₂.

TEMPERATURE 25° C.

Concentration gram atoms Na.	Amount solution titrated.	Amount HKSO ₄ required.		Amount sodium combined.	
		With ph. phth.	With meth. or.	As Na ₂ CO ₃ .	As NaHCO ₃ .
	c. c.	c. c.	c. c.	Per cent.	Per cent.
0.0044	50	0.10	2.3	8.7	91.3
	50	.10	2.3		
.0143	20	.30	3.0	20.0	80.0
	20	.30	3.0		
.0562	10	1.10	5.9	37.3	62.7
	10	1.10+	5.9		
.2248	10	7.0	23.6	59.3	40.7
	10	7.0	23.6		
.8847	2	6.15	18.65	64.0	36.0
	2	5.90	18.50		
	3	9.00	27.90		

¹ A solution containing 13.516 grams HKSO₄ per liter. The assumption is specifically made that the substance is a monovalent acid.

TABLE II.—*System: Na_2CO_3 , NaHCO_3 , and CO_2 .*

TEMPERATURE 37° C.

Concentration gram atoms Na.	Amount solution titrated.	Amount H_2SO_4 required.		Amount sodium combined.	
		With ph. phth.	With meth. or.	As Na_2CO_3 .	As NaHCO_3 .
	<i>c. c.</i>	<i>c. c.</i>	<i>c. c.</i>	<i>Per cent.</i>	<i>Per cent.</i>
0.0019	50	0.05	0.95	10.5	89.5
	50	.05	.95		
.0071	20	.15	1.45	21.1	78.9
	20	.15	1.40		
.0276	10	.55	2.75	41.3	58.7
	10	.60	2.78		
.1030	10	3.35	10.30	64.5	35.5
	10	3.30	10.30		
.421	2	3.50	8.45	81.9	18.1
	2	3.40	8.40		
.815	2	7.0	16.4	86.5	13.5
	2	7.1	16.2		
1.795	2+	15.1	36.1	83.4	16.6
	2	14.85	35.65		

TABLE III.—*System: Na_2CO_3 , NaHCO_3 , and CO_2 .*

TEMPERATURE 50° C.

Concentration gram atoms Na.	Amount solution titrated.	Amount H_2SO_4 required.		Amount sodium combined.	
		With ph. phth.	With meth. or.	As Na_2CO_3 .	As NaHCO_3 .
	<i>c. c.</i>	<i>c. c.</i>	<i>c. c.</i>	<i>Per cent.</i>	<i>Per cent.</i>
0.0017	50	0.1	0.9	22.2	77.8
	25	.05	.45		
.0071	20	.25	1.50	32.9	67.1
	20	.25	1.55		
.0266	10	.7	2.80	50.7	49.3
	20	1.45	5.65		
.1014	10	3.7	10.6	70.0	30.0
	10	3.75	10.7		
.4066	10	17.1	42.3	81.0	19.0
	2	3.5	8.6		
.8068	2	7.2	16.5	86.8	13.2
	2	7.0	16.15		
1.7486	2.1	15.9	36.5	87.1	12.9
	2	15.2	35.0		

TABLE IV.—*System: Na_2CO_3 , NaHCO_3 , and CO_2 .*

TEMPERATURE 75° C.

Concentration gram atoms Na.	Amount solution titrated.	Amount H_2SO_4 required—		Amount sodium combined.	
		With ph. phth.	With meth. or.	As Na_2CO_3 .	As NaHCO_3 .
	<i>c. c.</i>	<i>c. c.</i>	<i>c. c.</i>	<i>Per cent.</i>	<i>Per cent.</i>
0.003	50	0.2—	1.4	25.7	74.3
	25	.1	.7		
	25	.08	.7		
.019	20	.3	1.75	34.8	65.2
	20	.3	1.70		
.036	10	.9	3.3	55.7	44.3
	10	.95	3.35		
.270	5	4.9	12.5	79.5	20.5
	5	5.0	12.4		
.702	1	2.7	6.45	85.0	15.0
	1	2.75	6.5		
6.56	1	25.8	60.0	84.8	15.2
	1	25.5	61.0		

The results given in these tables are graphically presented in fig. 1.

It will be observed that the curves are all of the same general nature, that is, with increasing concentration the proportion of normal carbonate rapidly increases at first, but soon comes almost to a maximum and from that point on there is a very small increase in the proportion of normal carbonate with an increase in the total concentration. The higher the temperature the more nearly does the flat part of the curve lie parallel to the axis of abscissas, until at 100° C. practically the whole length of the curve is exactly horizontal to it. The curve plotted from the data obtained at 75° C. lies so close to that for 50° C. that it is not practicable to distinguish it from the latter on a chart of the scale represented in our figure.

For any given concentration the proportion of normal carbonate increases with the temperature, until at 100° C. for almost all concentrations the percentage of normal carbonate is practically 100; for

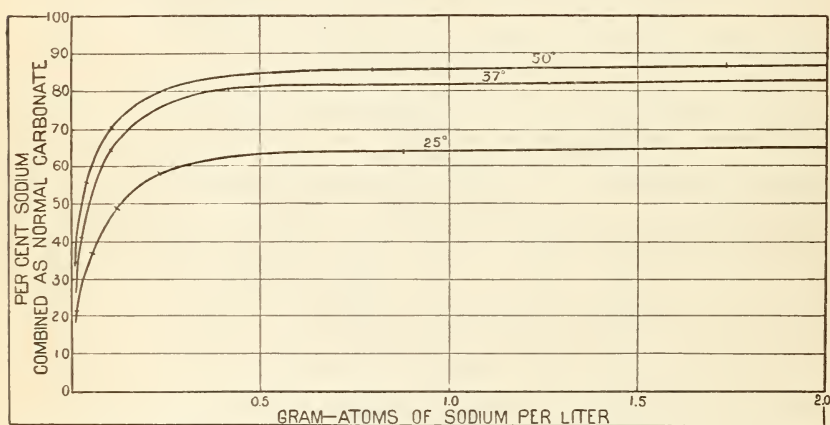


FIG. 1.—Diagram showing percentage distribution of sodium as carbonate and bicarbonate, at different concentrations and temperatures.

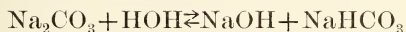
25° about 50 per cent of the sodium is in the form of normal carbonate when the total concentration is 0.12 to 0.13 gram-atoms of sodium per liter; with a concentration of 0.4 gram-atoms of sodium per liter about 63 per cent of the sodium is in the form of the normal carbonate; and there is a gradual increase from this point on, until at a concentration of 0.89 gram-atoms of sodium per liter about 64 per cent of the sodium is in the form of normal carbonate, and at a concentration of 8.0 gram-atoms of sodium about 86 to 87 per cent of the sodium is in the form of the normal carbonate. Similar data can readily be obtained for the other temperatures by interpolation on the charted curves.

A curious fact brought out by an inspection of the chart is, that at all temperatures there is a rapid increase in the percentage of normal carbonate up to a concentration of about 0.4 gram-atoms of sodium per liter, and from this point on the percentage of normal carbonate

increases very slowly; that is to say, a change from a rapid to a slow increase in the percentage of normal carbonate with increasing concentration comes at about the same concentration, irrespective of the temperature, at least below 75° C. What special significance, if any, this may have is not apparent at present.

By referring to Table IV it will be observed that in the solution containing 6.56 gram-atoms of sodium per liter there appeared to be actually a lesser percentage of the normal carbonates than in the solution containing 0.7 gram-atoms of sodium per liter. At first it was supposed that this indicated a faulty determination of the carbonates, and that the true interpretation of the result was that beyond a concentration of 0.7 gram-atoms of sodium per liter the curve for 75° C. was practically horizontal to the axis of abscissas. It appeared later, however, that in all probability, and at all temperatures, there is a maximum point on the curve beyond which there is an actual falling off in the percentage of normal carbonate with increased concentration of the solution. It is not possible to offer an explanation for this phenomenon at present, but it is intended to give the subject further attention at some future time.

It was hoped that possibly an approximation to the amount of hydrolyzation of sodium carbonate in solutions of varying concentration might be made from our results, by considering the amount of the hydrogen carbonate formed from the dissolved carbon dioxide as small and constant in amount on account of the small and constant partial pressure of this latter substance in the vapor phase. The nature of the curves at the lower concentrations, however, show conclusively that no such assumption can be made and that the influence of the dissolved carbon dioxide can not be disregarded. If the hydrolysis of the sodium carbonate be supposed to take place according to the scheme



then there must necessarily be as many reacting weights of sodium hydroxide in the solution as there are reacting weights of sodium hydrogen carbonate. But the curves vary continuously and without breaks, until at infinite dilution there is 100 per cent of the sodium in the form of hydrogen carbonate present and no sodium in the form of hydrate or normal carbonates. It is therefore apparent that the influence of the dissolved carbon dioxide, even though it be quite small in amount, can not be neglected, and the attempt to get a measure of the hydrolysis from the data here presented is vain. It may afford an explanation in part of why Walker and Cormack¹ found such a large proportion of HCO_3 ions as compared with CO_3 ions in their dilute solutions, and is probably the reason why they did not observe any hydrolysis of sodium hydrogen carbonate in dilute solutions.

¹ Loc. cit.

The data contained in Table I have been recalculated and are presented in Table V in another form. The first column gives the concentration in grams per liter with respect to the sum of the weights of normal carbonate and bicarbonate present; the second and third columns give the weight per liter and the percentage of normal carbonate present; the fourth and fifth columns, the corresponding data for the bicarbonate or hydrogen carbonate.

TABLE V.—System: Na_2CO_3 , NaHCO_3 and CO_2 .

TEMPERATURE 25° C.

Total salts dissolved.	Na_2CO_3 .		NaHCO_3 .	
	Weight.	Per cent.	Weight.	Per cent.
<i>Grams.</i>	<i>Grams.</i>		<i>Grams.</i>	
0.3555	0.0203	5.71	.3352	94.29
1.1053	.1505	13.62	.9548	86.38
4.0443	1.1041	27.30	2.9402	72.70
14.6558	7.0212	47.91	7.6346	52.09
56.3082	29.8223	52.88	26.5759	47.12

In fig. 2 these data are graphically presented, the ordinates representing the percentage of normal carbonate present and the abscissas the concentration with respect to the total salts present.

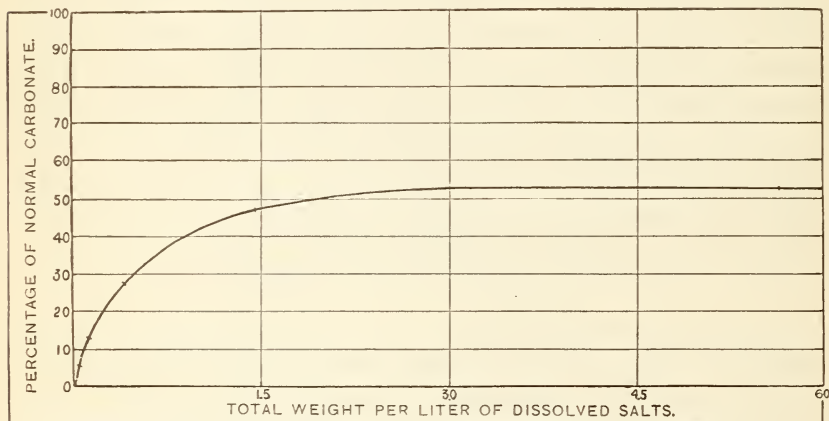


FIG. 2.—Diagram showing amounts of normal carbonate in solutions of the carbonate and bicarbonate of sodium.

An inspection of this curve shows that at 25° C. there are equal weights of sodium carbonate and sodium hydrogen carbonate in a solution in which the total weight of both salts is approximately 21.6 grams per liter, or 10.6 grams per liter of each. Even with a concentration with respect to both salts of 60 grams to the liter the amount of normal carbonate rises only to about 53.5 per cent of the total weight of the two salts present. The data obtained at 25° C. are presented in this form because it is much easier to make comparison with the data obtained in our experience in dealing with samples of alkali

soils and crusts, sent to the Division for examination, and with samples of water obtained from alkali areas. It is not proposed to go into this comparison in detail here. It will be discussed by Mr. Gardner¹ in connection with his work on the alkali areas in Utah. Suffice it to say that the results presented in this paper are very closely in accord with the data obtained from the experience of our field parties.

It has been amply demonstrated by Mr. Gardner that in the surface alkali of the Sevier Valley, Utah, the proportion of bicarbonate or hydrogen carbonate to normal carbonate is greatly increased as the total amount of these salts decrease. This same experience holds also for other cases, although it has not received such marked attention elsewhere. Further, an examination of the analytical results for the river water and the canal waters in the Sevier Valley shows results in very close accord with what would have been predicted on the basis of the work here described. It should be remembered, however, that the partial pressure of the carbon dioxide in the soil atmosphere is probably always greater, and generally much greater, than in the air. For this reason the equilibrium between the normal carbonate and hydrogen carbonate is displaced in the direction of the formation of more hydrogen carbonate, so that seepage water or spring water fresh from the soil will contain at first, or until sufficient time has elapsed for the solution to come to equilibrium with the air, much greater percentages of the hydrogen carbonate than our curve would indicate.

EXPERIMENTS WITH POTASSIUM SALTS.

In Table VI are given the results obtained from a series of experiments upon the equilibrium between the normal carbonate and hydrogen carbonate of potassium at 25° C. The increase of the percentage of normal carbonate with increasing concentration of potassium is not quite so rapid as in the case of the sodium salts for the lower concentrations, but is more rapid for higher concentrations than is the case with the sodium salts. The examination was extended to solutions of a higher concentration in this case to settle definitely the question of the existence of a maximum point in the curve. It unquestionably exists somewhere in the neighborhood of a concentration of two reacting weights of potassium per liter; beyond this point there appears to be a very gradual diminution of the percentage of normal carbonate.

¹Report, Field Operations of the Division of Soils for 1900, U. S. Dept. of Agr.

TABLE VI.—*System: K_2CO_3 , $KHCO_3$, and CO_2 .*

TEMPERATURE 25° C.

Concentration, gram-atoms K.	Amount solution titrated.	Amount $HKSO_4$ required—		Distribution of potassium.	
		With ph. phth.	With meth. or.	As K_2CO_3 .	As $KHCO_3$.
	c. c.	c. c.	c. c.	Per cent.	Per cent.
0.393	5	7.6	19.6	77.5	22.5
	5	7.65	19.75		
.553	2	4.75	11.0	83.9	16.1
	5	11.25	27.8		
1.025	2	8.9	20.5	86.8	13.2
	2	9.1	20.8		
	3	8.8	20.2		
1.865	2	17.1	37.1	91.4	8.6
	2	17.0	37.5		
2.820	2	25.2	56.4	89.0	11.0
	2	25.1	56.3		
3.710	2	33.15	74.2	88.6	11.4
	2	32.9	74.6		
4.31	1	19.3	43.0	89.6	10.4
	1	19.3	43.2		
5.695	1	25.25	56.9	88.7	11.3
	1	25.3	57.0		

The last two determinations given in the table do not appear quite consistent with the others. They were made subsequently to the others, smaller quantities of the solution being taken for the titrations and no special care being exercised to obtain great accuracy, as they were made solely for the purpose of establishing the fact that a maximum point would really exist on the curve. In a general way the phenomena presented by the potassium salts were so closely analogous to those presented by the sodium salts that it was not deemed advisable, from press of time, to continue the investigation of the former at higher temperatures at present.

THE CALCIUM SALTS.

The solubility of calcium carbonate in pure water at 16° C. is, according to Schlösing¹, about 0.0131 grams per liter. In such a solution Bodländer² has shown that in all probability about 80 per cent of the salt is hydrolized and dissociation is so complete that practically all the calcium in the solution is in the form of ions. With the addition of carbon dioxide to the vapor phase, however, the solubility of the calcium carbonate is much increased, owing to the formation of the more soluble calcium hydrogen carbonate. According to Schlösing³, at a partial pressure for the carbon dioxide in the gas phase of 0.9841 atmospheres, and at a temperature of 16° C., the solubility is increased so that there is the equivalent of 1.086 grams per liter of calcium carbonate in the solution. Treadwell and Reuter⁴ found that at 15° C. and under a partial pressure of the carbon dioxide in the

¹ Compt. rend., 74, 1552 (1872).² Zeit. für phys. Chem., 35, 28 (1900).³ Compt. rend., 75, 70 (1872).⁴ Zeit. für anorg. Chem., 17, 178 (1898).

gas phase equal to an atmosphere, the material dissolved was equivalent to 1.156 grams of calcium carbonate per liter. Under such conditions there could be no hydrolysis of the salts, and in the case of Treadwell and Reuter's experiment all the dissolved material must have been in the form of the hydrogen carbonate. The solubility of the calcium is certainly increased nearly ninety times.

In the case of soil solutions the partial pressure of the carbon dioxide must be somewhere between the limits 0.0 and one atmosphere, and the solubility of calcium carbonate will be somewhere between the extremes noted above. An approximation to its solubility in solutions in contact with the air can be obtained from Schlösing's figures. This authority found that at 16° C., and a pressure for the carbon dioxide equal to 0.000504 atmospheres, the solubility was 0.0746 grams per liter—calculating the salt as normal carbonate—or in effect the solubility is nearly six times what it would be in pure water.

But another aspect of the question must be borne in mind in this connection. Treadwell and Reuter have definitely shown that calcium hydrogen carbonate in aqueous solution is a rather stable compound, at least at 15° C., and that it does not always decompose at once with the partial inversion to the normal carbonate as the partial pressure of the carbon dioxide in the vapor phase is lowered. They found that after reducing the partial pressure of the carbon dioxide in the gas phase to zero, there remained no free carbon dioxide in the solution, but that the solution still contained an amount of calcium, entirely in the form of hydrogen carbonate, equal to 0.3850 grams per liter of this salt. This would be equivalent to 0.2380 grams per liter of the normal carbonate or 18.16 times the amount found soluble in pure water by Schlösing. Therefore the origin and past history of a solution is of the utmost importance in considering its concentration with respect to calcium carbonate or hydrogen carbonate. For example, a solution which has been formed in a soil in which there is a large amount of carbon dioxide, and which subsequently comes to equilibrium with the air, may well be very different in concentration from a solution which was formed directly in contact with the air. It is probable, however, that with agitation of the solution, such as would occur in a turbulent stream, for example, the stability of the calcium hydrogen carbonate would be considerably lessened, and that it would partially decompose, the concentration being reduced to the point which would result from the solution of calcium carbonate by water in contact with air.

The experiment has been made in the laboratory of this Division of preparing two solutions of calcium carbonate—one made by dissolving the calcium carbonate in distilled water from which the dissolved carbon dioxide has been expelled by boiling, the other by dissolving the salt in distilled water containing somewhat more carbon dioxide than would be dissolved from the air. A few drops of alcoholic solu-

tion of phenolphthalein were added to each. The first showed an intense red color, but the second showed no color, indicating that there was practically no hydrolized base in the solution. A current of air was passed through both solutions continuously for three days. Aliquot portions of both solutions gave practically identical results for calcium determinations. After the passage of the air through the solutions had been stopped they both showed a faint trace of pink color on the addition of phenolphthalein. The amount of material in solution was so small that it did not seem worth while to attempt very accurate measurements, but the mean of two closely agreeing series of titrations indicated that at 30° C. in equilibrium with the air not more than 3 per cent of the calcium present could be combined as normal carbonate. At lower temperatures and lesser concentrations the percentage of normal carbonate must be even less. It did not seem advisable, therefore, to attempt any further study of the distribution of the base calcium between the normal carbonic acid and the hydrogen carbonic acid in solutions of these salts in equilibrium with atmospheric air, or in equilibrium with a gas phase containing a larger proportion of carbon dioxide than ordinary air.

The facts just presented are of very great importance in geological and soil studies, for it is evident that with solutions such as we have been discussing one is dealing almost entirely with calcium hydrogen carbonate; and in the reactions with other electrolytes which may come into the solution it is the hydrogen carbonate which must be considered.

Another interesting point is that although a solution may be holding as much of this salt as is possible under existing conditions it can not be considered as saturated with respect to it, for it may be able to take up more of the salt by increasing the partial pressure of the carbon dioxide in the gas phase. It would be interesting to know what the absolute solubility of calcium hydrogen carbonate is for some temperatures. It is probable that it is considerable in amount, and it is not so surprising that deep-seated waters are able to carry such relatively large quantities of this salt. The much increased solvent action of waters carrying much dissolved carbon dioxide upon calcium-bearing rocks is readily intelligible in the light of these facts.

THE MAGNESIUM SALTS.

The solubility of magnesium carbonate in pure water at 12° C. is given by Engel¹ as 0.970 grams per liter. Treadwell and Reuter² found the solubility at 15° C., in contact with a vapor phase in which the partial pressure of the carbon dioxide had been reduced to zero, to be about 0.627 grams per liter. These investigators found that under a partial pressure for the carbon dioxide equal to one atmosphere there was in solution 12.105 grams per liter of the magnesium hydro-

¹ Compt. rend., 100, 144 (1885); Ann. Chim. et Phys. (6), 13, 349 (1888).

² Zeit. für anorg. Chem., 17, 199 (1898).

gen carbonate—equivalent to 6.977 grams per liter of the normal carbonate. Unlike the corresponding calcium salt, they found the magnesium hydrogen carbonate to be very unstable, and that all the magnesium could remain in the form of this salt only when there was a considerable excess of carbon dioxide dissolved in the solution.

Every investigator who has attempted to study magnesium carbonate in solution has experienced very great experimental difficulties. There is good reason to believe, as Bodländer¹ has pointed out, that these difficulties are due to the formation of complex molecular species $n\text{Mg}(\text{OH})_2 \cdot m\text{MgCO}_3$, with complex ions, resulting in the presence of considerable quantities of hydroxyl ions in the solution. This is tantamount to saying that there is considerable hydrolized normal carbonate in the solution—a fact which is apparent when one adds phenolphthalein to a solution of magnesium carbonate.

In saturated solutions of magnesium carbonate the formation of these complex compounds is of undoubted importance, and their study, as has been said above, is exceedingly difficult. In all probability they are mainly responsible for the discrepancies in the observations of various investigators of this subject. But in solutions of lesser concentration, and especially when there is some excess of dissolved carbon dioxide, they do not assume any practical importance even if they have an actual existence under such circumstances. To all intents and purposes the solution may be considered as containing only the solutes normal magnesium carbonate (with the hydrolized free base) and magnesium hydrogen carbonate. It appears worth while, therefore, to get some idea as to the distribution of the base between the two acids by the method described in connection with the work on the sodium salts. The results are given in Table VII, which is self-explanatory.

TABLE VII.—*System: MgCO_3 , $\text{Mg}(\text{HCO}_3)_2$ and CO_2 .*

TEMPERATURE 30° C.

Total Mg (grams per liter).	Mg as MgCO_3 (grams per liter).	Mg as $\text{Mg}(\text{HCO}_3)_2$ (grams per liter).
0.02410	0.01205	0.01205
.13135	.06820	.06314
.16087	.08676	.07411

Total Mg (gram atoms per liter).	Mg as MgCO_3 .	Mg as $\text{Mg}(\text{HCO}_3)_2$.
0.00100	<i>Per cent.</i> 50.00	<i>Per cent.</i> 50.00
.00545	51.92	48.08
.00667	53.93	46.07

¹ Zeit. für phys. Chem., 35, 31 (1900).

TABLE VII.—*System: $MgCO_3$, $Mg(HCO_3)_2$ and CO_2 —Continued.*

TEMPERATURE 30° C.

Total salts in solution (grams per liter).	Normal carbonate.		Hydrogen carbonate.	
	Grams per liter.	Per cent.	Grams per liter.	Per cent.
0.1144	0.0418	36.5	0.0726	63.5
.6174	.2368	38.2	.3806	61.7
.7479	.3012	40.3	.4467	59.7

Assuming that at infinite dilution all the magnesium will be in the form of hydrogen carbonate, it is evident that the curve for the more dilute solutions is much steeper than the curve for the corresponding concentrations with respect to the sodium salts. But the general nature of the curve will be the same, the upper part being very flat. It would appear probable, therefore, that in all solutions of the magnesium salts with which one has to deal practically, and which are in equilibrium with the air but not in contact with the magnesium carbonate in the solid phase, about 50 per cent (in round numbers) of the magnesium is in the form of the normal carbonate. Solutions of the magnesium salts are therefore in strong contrast to solutions of the calcium salts where practically all the base is combined in the form of the hydrogen carbonate.

But in contact with the magnesium carbonate in the solid phase quite different conditions may obtain when there is also an excess of carbon dioxide in the solution. Some carefully prepared magnesium carbonate was suspended in distilled water and a current of air, which had previously been washed in a dilute solution of sulphuric acid, was passed through continuously for twenty-nine days. The solution then contained 0.1530 gram of magnesium per liter, of which 0.0446 gram of magnesium per liter, or 29.1 per cent of the total, were in the form of the normal carbonate. The current of air was then passed through the solution for seventeen days longer. The solution then contained 0.1837 gram per liter of magnesium, of which 0.0542 gram, or 29.5 per cent, were in the form of normal carbonate. The flask containing the solution and suspended solid magnesium carbonate was then put aside for fifty-four days longer. The solution was then found to contain 0.1808 gram of magnesium per liter, of which 0.0615, or 33.9 per cent, were combined as normal carbonate.

The total amount of magnesium in the solution, as shown by the last determination, is equivalent to 0.6276 gram normal carbonate per liter, which agrees with the figure (0.627) obtained by Treadwell and Reuter,¹ although the mean temperature of the solution in the experiments here described was about 22° C. instead of 15° C., the temperature at which the investigators quoted worked. Moreover the solution of

¹ Zeit. für anorg. Chem., 17, 199 (1898).

Treadwell and Reuter was supposed to contain no free carbon dioxide or carbonic acid.

From the data which have been presented above, it would appear that in a solution near the saturation point and in equilibrium with atmospheric air, upwards of 50 per cent of the magnesium would be in the form of the normal carbonate. When the solution was brought in contact with the salt in the solid phase and allowed to remain in equilibrium with atmospheric air more of the substance would go into solution (as the hydrogen carbonate) until the proportion of the base combined as normal carbonate would fall to about 34 per cent or lower. These facts are of the utmost importance in the consideration of "alkali" problems, for there is evidently a marked difference in this respect as well as in total solubility between the carbonates of calcium and of magnesium. It seems probable, therefore, that the presence of much magnesium carbonate, as compared with calcium carbonate, in the soil would have a much more marked effect in producing soluble normal carbonates or the dreaded "black alkali." These views appear to be in perfect accord with the observations of the field parties of this Division. It should be borne in mind that soil solutions in general carry much more dissolved carbon dioxide or carbonic acid than solutions in equilibrium with atmospheric air; and in such solutions the relative percentage of the magnesium in the form of normal carbonate may well be much less than what has just been considered in the foregoing paragraphs.

Another point to which it seems worth while to call attention here, and which is well illustrated by the experiments described above, is the comparatively long periods of time required to bring a solution to equilibrium with a solute in the solid phase, when the solute is sparingly soluble. Attention has been called to this in connection with some other investigations made in this Division, and it must be insisted that this is an important matter in considering soil phenomena, although a factor most difficult to control and for which to make proper allowance.

SUMMARY.

From the facts presented in this paper the following conclusions are drawn:

1. When in equilibrium with air every aqueous solution of sodium normal carbonate contains necessarily some sodium hydrogen carbonate. And, conversely, every solution of sodium hydrogen carbonate contains necessarily some normal sodium carbonate. At equilibrium there is a definite distribution of the base between the two acids.

2. The equilibrium is conditioned by the concentration, the temperature, and the partial pressure of the carbon dioxide in the vapor phase.

3. At any given concentration the proportion of normal carbonate

increases with rise of temperature. Conversely at any given temperature the proportion of normal carbonate increases with the total concentration except at any great concentration.

(4) The phenomena presented by the solutions of the carbonate and hydrogen carbonate of potassium are strictly analogous to those presented by the sodium salts, differing only in the quantitative relations.

(5) Above some concentrations, relatively large, there is a gradual diminution of the percentage of normal carbonate; that is, there is an actual maximum point to the curve. The significance of this maximum point is not understood at present.

(6) It seems improbable that more than 3 per cent of the calcium is ever combined as the normal salt in solutions of the carbonates of this base when in contact with a vapor phase containing as much or more carbon dioxide than atmospheric air. Practically one has to consider only solutions of the hydrogen carbonate.

(7) Solutions of the carbonates of magnesium are in marked contrast to those of the calcium salts. When the partial pressure of the carbon dioxide in the gas phase is not less than in atmospheric air upward of 50 per cent of the base may be combined as normal carbonate, if the solution is not in contact with the salt in the solid phase; the percentage falls below 35 per cent when in contact with the solid normal carbonate. Both normal carbonate and hydrogen carbonate are to be considered in dealing with solutions of the magnesium salts.

(8) The formation of soluble normal carbonates or "black alkali" would take place to a greater extent in the presence of magnesium carbonate than in the presence of calcium carbonate alone in the soil.

(9) The observations and conclusions presented in this paper are in thorough accord with the experiences of the field parties of this Division

SOLUBILITY OF GYPSUM IN AQUEOUS SOLUTIONS OF SODIUM CHLORIDE.

By FRANK K. CAMERON.

INTRODUCTION.

The effect of one electrolyte in determining the solubility of another in water solutions has received considerable attention from investigators within the past few years. This work has been directed mainly to a verification of theories deduced from applications of the mass law to electrolytic dissociation and quite satisfactory results have been obtained for very dilute solutions.

Excepting the early classical researches of Kopp,¹ Karsten,² Rüdorff,³ and Engel,⁴ but little satisfactory work is to be found described in the literature on this subject when concentrations of any magnitude were involved or when the work was carried on through any great range of concentration. Moreover, the cases thus studied have been carefully selected so as to take advantage of some peculiar characteristic of one or more of the components in the system under consideration and thus simplify the theoretical formulation of the factors involved. Such cases as one meets most frequently in everyday practice—two strong electrolytes in water, for example—have received but scant attention. The reason for this is that such cases *a priori* could not be expected to give satisfactory results, so far as the theories under examination were concerned, it being a well-established fact that for such electrolytes the dissociation does not take place in accordance with the *mass law*, as we now formulate it. This point will be referred to again.

For a correct understanding of the "alkali" problem of the arid regions, such a problem as occurs in many of our Western States, this mutual influence of salts or electrolytes in solution is of very great importance. Qualitatively we already know something in this

¹ Ann., 34, 260 (1840).

² Abhandl. der Berlin Akad. (1841).

³ Pogg. Ann., 148, 456, 555 (1873). Wied. Ann., 25, 626 (1885).

⁴ Compt. rend., 102, 113 (1886).

connection, but quantitative data have been almost entirely wanting up to the present.¹

We have to do here with solutions often far from dilute, and we have no consistent theory to guide us; furthermore, the particular salts involved in the "alkali" problem have not commended themselves to investigators.

It is seldom that we have to deal with but one pair of electrolytes and their metathetical products in the study of an "alkali" problem, but in the absence of any available data it was deemed wise to take a case of this kind for a preliminary study. Accordingly, from time to time, as attention to other work of the laboratory permitted, the solubility curves for several pairs of electrolytes have been followed quantitatively. Some results are here recorded for the system: Water, calcium sulphate, sodium chloride, and their reaction products.

DESCRIPTION OF EXPERIMENTS.

Solutions of sodium chloride of various concentrations were prepared. The sodium chloride used was chemically pure material obtained from Eimer and Amend and tested by analyzing for chlorine with very satisfactory results. Into these sodium chloride solutions an excess of calcium sulphate in the form of finely divided gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was introduced, and the solutions then allowed to stand, with frequent shakings, from one to fourteen days, according to the temperature at which the work was being done, in order that equilibrium might be reached. The gypsum used in the experiments described in this paper was from two sources. One sample was a very finely powdered gypsum obtained from Hot Springs, Fall River County, S. Dak., an analysis of which gave very satisfactory results for the formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The material was powdered so finely that it displayed a decided tendency to "cake," and when used the solutions had to be shaken frequently. This "caking" did not resemble the setting of plaster of paris, but the substance behaved more like a plastic clay. The other gypsum sample was obtained by pulverizing in an agate mortar some very fine crystals of gypsum kindly furnished by Mr. Wirt Tassin, of the United States National Museum. It may be said at once that curves were plotted from data

¹ For a review of the earlier work see W. W. J. Nicol (*Phil. Mag.*, **31**, 369 (1891)) and J. E. Trevor (*Phil. Mag.*, **32**, 75 (1891)). More recent investigations of interest in this connection are the Solubility of calcium bicarbonate in sodium chloride solutions, Treadwell and Reuter (*Zeit. für anorg. Chem.*, **17**, 192 (1898)); Solubility of gypsum in solutions of hydrochloric acid and calcium chloride, Lunge (*Jour. Soc. Chem. Ind.*, **4**, 31 (1885)); Solubility of gypsum in solutions of ammonium chloride, magnesium chloride, and calcium chloride, Tilden and Shenstone (*Proc. Roy. Soc.*, **38**, 335 (1885)); Solubility of calcium sulphate in several acids, Ostwald and Banthisch (*Jour. für prak. Chem.* [2], **29**, 52 (1884)).

obtained with both these materials and with calcium sulphate obtained by precipitation from mixing solutions of calcium chloride and sodium sulphate, all of which agreed most satisfactorily. The material first described possessed one advantage in that its very finely divided condition enabled it to go into solution more rapidly and greatly shortened the time required to obtain final equilibrium in the system.

Preliminary experiments indicated the advisability of using rather large volumes of solution. About 300 cubic centimeters were found to be a very convenient amount. In the experiments at higher temperatures the portions of solutions required for analysis were drawn off with a pipette as quickly as possible, care being taken to avoid drawing off any solid gypsum. In some cases considerable difficulty was experienced in this respect, but it is not believed that any of the results here presented are open to criticism on this account. When working at the lower temperatures, a 100 cubic centimeter portion was filtered through a "Schleicher und Schüll" folded filter, discarding the first runnings. This 100 cubic centimeter portion was then diluted to 500 cubic centimeters, and aliquot parts taken for the analytical determinations. The chlorine was determined by titrating with a carefully standardized silver nitrate ($N/10 \text{ AgNO}_3$) solution, using potassium chromate as indicator. The sulphates were estimated gravimetrically as barium sulphate, in the usual manner. In some cases the calcium was also determined, but as nothing especial was thus gained this last procedure did not seem to be advisable.

For a constant temperature bath a large washtub filled with water was used. With such a large volume of water the temperature changed quite slowly, and by passing in a stream of water or steam, as the case might be, no serious difficulty was experienced in keeping a temperature constant within a degree or a degree and a half Celsius. To attempt greater accuracy in this direction was not justifiable in view of the results obtained, and the advantage derived in being able to work with large volumes of solution in a bath of this size far outweighed any disadvantage arising from a variation in the temperature of the magnitude described.

DETERMINATIONS MADE AT 15° C .

The first series of determinations obtained were made at 15° C . They are given in Table VIII, in which the first column contains the amounts of sodium chloride in the solution, assuming all the sodium and chlorine to be thus combined, and the second column containing the corresponding amounts of calcium sulphate found to be soluble. A much more complete set of determinations was then made at 23° .

TABLE VIII.—*Solubility of calcium sulphate in aqueous solutions of sodium chloride at 15° C.*

Grams NaCl per liter.	Grams CaSO ₄ per liter.
0.6	2.3
1.1	2.5
5.1	3.1
10.6	3.7
31.1	4.8
51.4	5.6
139.9	7.4

TABLE IX.—*Solubility of calcium sulphate in aqueous solutions of sodium chloride at 23° C.*

Grams NaCl per liter.	Reacting weights NaCl per liter.	Grams CaSO ₄ per liter.	Reacting weights CaSO ₄ per liter.	Grams gypsum per liter.
0.99	0.0171	2.37	0.0176	2.99
4.95	.0852	3.02	.0223	3.82
10.40	.1790	3.54	.0262	4.48
30.19	.5200	4.97	.0368	6.31
49.17	.8471	5.94	.0439	7.51
75.58	1.3018	6.74	.0499	8.53
129.50	2.2314	7.50	.0555	9.42
197.20	3.3968	7.25	.0536	9.17
229.70	3.9568	7.03	.0520	8.88
306.40	5.2785	5.68	.0420	7.19
a 315.55	a 5.4948	a 5.37	a .0397	a 6.79

a The solution in this case was in contact with both gypsum and sodium chloride in the solid phase.

DETERMINATIONS MADE AT 23° C.

The data given in Table IX are the results of experiments made with more than ordinary care. The calcium sulphate used was prepared by pulverizing selected gypsum crystals. Other series made at this temperature with calcium sulphate from various sources showed most satisfactory agreements, and it is not deemed worth while to present them here. The results given in this table are presented graphically in fig. 3. The ordinates represent grams gypsum per liter of solution, and the abscissas grams sodium chloride per 100 cubic centimeters. For convenience in reference, the corresponding values in reacting weights and in anhydrous calcium sulphate are also given in the table. No advantage is evident in charting the curve in terms of these latter quantities, it being merely displaced somewhat thereby without changing its general nature, and the form in which it is presented promises greater usefulness to the work of this Division.

By referring to fig. 3 it will be observed that the solubility of the calcium sulphate or gypsum reaches a maximum in solutions containing about 135–140 grams of sodium chloride per liter, upward of 7.5 grams calcium sulphate—equivalent to 9.3 grams gypsum—being dis-

solved at this concentration, against approximately 2 grams calcium sulphate, equivalent to 2.7 grams gypsum soluble in pure water.

In view of the generally accepted ideas on the mutual effect of electrolytes in solution, the existence of this maximum solubility point was entirely unexpected and surprising.¹ The data given are calculated with reference to a constant volume of solution. It seemed possible that the relatively large amounts of salts present in the more concentrated solutions had replaced so much of the volume of the solvent in this constant volume of solution that the existence of this maximum solubility was only apparent and not real. Experiments to test this point will be described presently.

It was deemed advisable to determine experimentally whether or not the composition of the solid phase, containing both sodium chloride and gypsum, would affect the composition of the solution in contact with it. Therefore two mixtures, containing, respectively, 45 grams of sodium chloride with 1 gram of gypsum and 45 grams of sodium

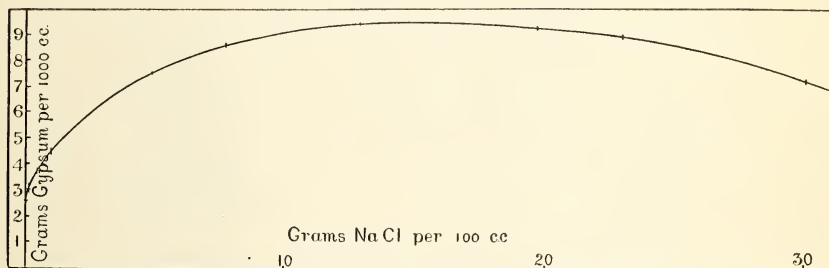


FIG. 3.—Diagram showing the solubility curve for gypsum in solutions of sodium chloride.

chloride with 10 grams of gypsum, were each brought into contact with 100 c. c. of distilled water. The mixtures were shaken continuously for four days, then placed in the constant-temperature bath and allowed to settle. An analysis of the supernatant solutions gave identical results for both cases. As there was no reason *a priori* to expect a different result with this pair of electrolytes no further experiments on this point were deemed necessary.

DETERMINATIONS MADE AT HIGHER TEMPERATURES.

In Table X the data obtained at higher temperatures are given. The results are not presented in graphic form because the curves would lie so close together, when plotted on any convenient scale, as to fail to bring out more clearly than the tables do any points especially worth noting.

¹ It had been observed, however, by Tilden and Shenstone, *Proc. Roy. Soc.*, **38**, 335 (1885).

TABLE X.—*Solubility of calcium sulphate in aqueous solutions of sodium chloride at various temperatures.*

30° C.		70° C.	
Grams NaCl per liter.	Grams CaSO ₄ per liter.	Grams NaCl per liter.	Grams CaSO ₄ per liter.
0.5	2.5	0.5	2.2
10.3	3.6	10.0	3.4
30.3	5.0	29.6	4.9
47.3	6.1	48.8	5.8
73.4	6.9	132.7	7.4
126.9	7.3	195.0	7.6
192.4	7.7	-----	-----
52° C.		82° C.	
Grams NaCl per liter.	Grams CaSO ₄ per liter.	Grams NaCl per liter.	Grams CaSO ₄ per liter.
0.5	2.3	0.0	2.07
1.1	2.4	1.0	2.18
5.0	2.9	5.0	2.65
10.1	3.5	10.1	3.30
29.6	5.0	29.5	4.68
48.3	5.8	48.8	5.54
75.7	6.6	74.9	6.23
131.6	7.1	128.7	7.00
195.9	7.4	195.1	7.51

By referring to the tables it will be observed that the curve for 30° C. would lie above that for 23° for the most part, but the curves

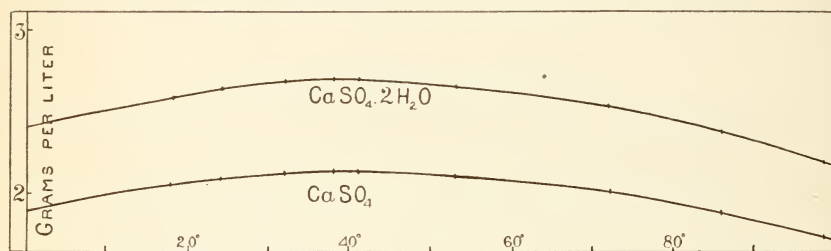


FIG. 4.—Diagram showing the solubility curves for calcium sulphate at various temperatures. Plotted on the basis of gypsum and the anhydrous salt.

for 50° and the higher temperatures, respectively, would fall lower and lower on the chart. At first sight this might be attributed to the fact that gypsum shows a maximum solubility in pure water at about 37.5° C., as may be seen by referring to fig. 4, plotted from Marignac's results.¹ But that this fact alone is not sufficient to account for the results noted seems probable when it is observed that the solubility of the gypsum in the sodium chloride solutions, even at 80°, may be increased to nearly 3.5 times its solubility in pure water, whereas the solubility of the calcium sulphate in pure water at 37.5°, the maximum point, is about 1.119 times its solubility at 0°, and about 1.243 times its solubility at 99°, as calculated from Marignac's data. That a causal relation exists between the facts observed is to be expected, but what it may be is not obvious at present.

¹ Ann. Chim. et Phys. (5) 1, 274 (1874).

As far as was observed, the curves determined at temperatures above 30° C. were asymptotic, and did not show the existence of "maximum" points. That such points may exist is of course possible, but if so they must lie near the points indicating the extreme solubility of sodium chloride in the system. The labor involved in attempting to locate them did not appear to be justified at the time the curves were determined, and the purposes for which this investigation was undertaken has not since indicated the desirability of a more exhaustive examination for them.

DETERMINATIONS MADE AT 26° C.

In this series the determinations were made on solutions of the volume of a small pycnometer or specific gravity bottle, and in each case the actual weight of the solutions was determined. Having determined the weights of the salts present, the weights of water actually present as solvent were then calculated by subtracting the weights of the salts present from the total weights of the solutions.

The volume of the pycnometer at 26° was carefully determined by boiling it for some time in distilled water, cooling to 26°, weighing it filled, carefully drying, and weighing it empty. The data obtained follows:

	Grams.
Weight of pycnometer filled	135.5364
Weight of pycnometer empty	35.7956
Weight of water	99.7408

The density of water at 26° being taken as 0.99687,¹ the volume of the pycnometer was 100.05 cubic centimeters; therefore no attempt was made to correct the data obtained to the basis of 100 cubic centimeters, the variations being very probably within the limits of error of the methods used.

Table XI contains data obtained from experiments made at 26° C. A comparison of the data in Table XI with that in Table IX shows a very satisfactory agreement between the two series of determinations made at 23° and 26°, respectively.

TABLE XI.—*Solubility of calcium sulphate in aqueous solutions of sodium chloride at 26° C.*

Grams solution per 100 c. c.	Grams water per 100 c. c.	Grams NaCl per 100 c. c.	Grams CaSO ₄ per 100 c. c.
99.9848	99.7727	0.0000	0.2121
106.4441	96.6631	9.1154	.6656
109.8113	94.6945	14.3089	.7179
110.1215	94.5708	14.8343	.7164
111.9622	93.6001	17.6502	.7119
114.8826	91.3276	22.8756	.6794
117.0720	90.0049	26.4173	.6498
120.3439	87.7233	32.0491	.5715

¹Smithsonian Physical Tables, Gray, p. 94 (1896).

NATURE OF THE CURVE REFERRED TO A CONSTANT WEIGHT OF
SOLVENT.

From the results given in Table XI were calculated those given in Table XII; that is to say, the amounts of calcium sulphate in a solution saturated with respect to it and the corresponding amounts of sodium chloride when the solution contains exactly 100 grams of water and irrespective of whatever volume the solution might have.

TABLE XII.—*Total NaCl and CaSO₄ in water at 26° C.*

NaCl per 100 grams water.	CaSO ₄ per 100 grams water.
0.0000	0.2126
9.4307	.6886
15.2056	.7581
15.6859	.7575
18.8570	.7605
25.0478	.7439
29.3509	.7219
36.5343	.6515

From this table it will be seen that a well-marked maximum solubility point does exist. This point corresponds in round numbers to

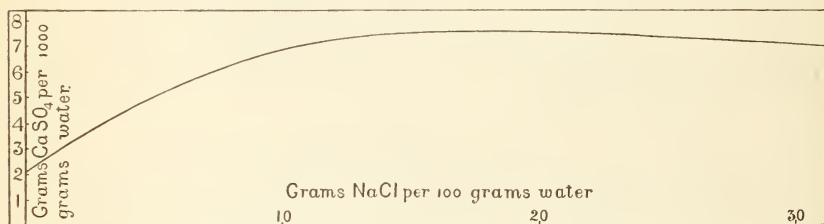


FIG. 5.—Diagram showing the solubility curve for calcium sulphate in solutions of sodium chloride. Results given in terms of grams present in a constant weight of water.

0.76 gram of calcium sulphate and 15.3 grams sodium chloride in 100 grams of water. The sixth determination shows an apparent discrepancy, but this is probably due to an inaccurate weighing of the solution, since the data of Table XI agree so well with the very carefully established data in Table IX.

The data given in Table XII are represented graphically in fig. 5, from which the general nature of these solubility changes is readily apparent.

Tilden and Shenstone¹ obtained similar results for this pair of electrolytes working at 20° C. The curve obtained by them follows very closely the curve given here, but lies somewhat above. Nevertheless, it is believed that the results given here are the more reliable, as they have been repeated several times and with great care. The maximum point on Tilden and Shenstone's curve would be displaced somewhat

¹Proc. Roy. Soc., 38, 335 (1885).

further to the right than in the curve here given. It seems possible that the discrepancies between the two curves at highest concentration might disappear if they could be compared on exactly the same basis; but the statement of the results of the authors quoted is somewhat vague on this point, and it is not quite certain on what basis their results were computed.

SOLUBILITY CHANGES FOR GYPSUM WITH VARYING TEMPERATURE.

Above 37° to 38° the solubility of gypsum in pure water decreases with rising temperature, and, as will be seen from Marignac's¹ results, given in Table XIII and plotted in fig. 5, at a point a little above 80° the solubility becomes less than at any lower temperature.

TABLE XIII.—*Solubility of gypsum in water at various temperatures.*

Temperature.	Calculated for gypsum.		Calculated for calcium sulphate.	
	Parts water required to dissolve one part $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.	Grams $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ dissolved by a liter of water.	Parts water required to dissolve one part CaSO_4 .	Grams CaSO_4 dissolved by a liter of water.
0.....	415	2.41	525	1.90
18.....	386	2.59	488	2.05
24.....	378	2.65	479	2.09
32.....	371	2.70	470	2.13
38.....	368	2.72	466	2.15
41.....	370	2.70	468	2.14
53.....	375	2.66	474	2.11
72.....	391	2.56	495	2.02
86.....	417	2.40	528	1.89
99.....	451	2.22	571	1.75

From the data presented above it would appear that the solubility of gypsum follows the same general law when sodium chloride is present, up to a concentration for this latter salt of about 135–140 grams per liter of solution. The figures of Tilden and Shenstone² for the solubility of gypsum in a 25 per cent solution of ammonia chloride indicate that while a maximum solubility point is reached with rising temperature it lies at or above 60° C. It seems very desirable, however, that their results for this particular case should be repeated before much weight be given them. On the other hand, they showed that when the gypsum was dissolved in solutions of calcium chloride, in which case the two substances furnish a common ion, that the solubility steadily increased without the appearance of any maximum solubility point, at least as far as 94° C.

¹ See also Goldammer, *Chemisch. Centralb.*, p. 708 (1888), whose results indicate a maximum solubility for gypsum in water at about 37.5° C., while Poggiale, *Ann. de Chim. et Phys.* (3), 8, 469 (1843), found it to be at 35° C.

² *Proc. Roy. Soc.* 38, 335 (1885).

CHANGE IN DENSITY OF THE SOLVENT.

In the course of experiments for the solubility curve at 26° C. the fact was brought out that calcium sulphate dissolved in water caused a contraction of the solvent, as will be seen from the following figures:

	Grams.
Weight of pycnometer filled with water at 26° C	135.5167
Weight of pycnometer empty	35.7965
Weight of water	99.7202
Weight of pycnometer filled with solution of calcium sulphate saturated at 26° C	135.7813
	35.7965
Weight of solution	99.9848
Weight of calcium sulphate2121
Weight of water as solvent	99.7727
Weight of water alone	99.7202
	.0525

In other words, although a portion of the volume of the water was displaced by the calcium sulphate in solution, the water as solvent weighed 0.0525 grams more. Therefore there must have been an actual condensation of the solvent. The fact that such a condensation does take place as a rule when salts are dissolved in water has been known for some time, and Nernst¹ has suggested that this fact may possibly be connected with the phenomena of electrolytic dissociation, but as yet the nature of this connection has not been ascertained. The experiment was repeated with results agreeing fairly well with those given, but as the temperature was not noted it is not considered worth while to present them here. The water used in the experiments just described was not boiled. But if we take the results given on page 31 we have the following data for 26° C.:

	Grams.
Weight of pycnometer with water	135.5364
Weight of pycnometer empty	35.7956
Weight of water (boiled)	99.7408
Weight of water as solvent	99.7727
	.0319

From these figures it would appear that the condensation was somewhat less than the first figures indicated, and that it would be worth while to redetermine the condensation by boiling both the pure water and the solution. This was done, but owing to a misunderstanding the determinations were made at 31° C. instead of 26° C. The weight of calcium sulphate taken was not determined directly, but was

¹Theoretical Chemistry (translated by Palmer), p. 332, 1893.

obtained by interpolation on the curve plotted from Marignac's results.

	Grams.
Weight of pycnometer filled with water	135.4241
Weight of pycnometer empty	35.7965
Weight of water (boiled)	99.6276
Weight of pycnometer filled with solution	135.7344
Weight of pycnometer empty	35.7965
Weight of solution (boiled)	99.9379
Weight of calcium sulphate2130
Weight of water as solvent	99.7249
Weight of water (boiled)	99.6276
	.0973

From the figures just presented the density of the calcium sulphate solution will be 1.0031 at 31° when compared with water at the same temperature. Making the assumption that the air dissolved in both solution and in water alone was the same, the density at 26° would be 1.0026. It is given as 1.0022 at 15° by Stolba.¹ It would be interesting to compare these values by the methods of Valson² and Bender.³ But a saturated solution of calcium sulphate is only about a hundred and fiftieth normal (N/150), and in consequence we have not been able to find any data already determined and suited to this purpose.

COMPOSITION OF THE HYDRATE OF CALCIUM SULPHATE IN CONTACT WITH SOLUTIONS.

It has frequently been necessary in the work of the laboratory to heat solutions containing calcium and sulphuric acid salts to temperatures higher than 80° , and the frequent precipitation of calcium sulphate under these circumstances had raised the suspicion that possibly some other hydrate of calcium sulphate than the dihydrate was formed at this temperature.

The suspicion was strengthened by the frequently observed fact that when solutions containing calcium sulphate and other salts were evaporated to dryness the residue apparently would not redissolve in the amount of water originally present. A microscopic investigation of this apparently insoluble residue left but little doubt that it was composed entirely of small gypsum crystals. These might of course have resulted from another hydrate on standing at a temperature at which the dihydrate was the stable form; but this would have assumed a high speed of transformation, as in some cases the microscopic examination was made as soon as possible after removing the material from the steam bath.

Hoppe-Seyler observed that gypsum lost water when heated to

¹ Jour. prakt. Chem., 97, 503 (1866).

³ Wied. Ann., 20, 560 (1883).

² Compt. rend., 73, 441 (1871); 77, 806 (1873).

120°–130° in contact with saturated solutions of sodium chloride or calcium chloride. Rose¹ observed the same phenomenon when the gypsum was heated in contact with a solution of sodium sulphate, although he doubted if it took place with a solution of sodium chloride.

Three 100 cubic centimeter measuring flasks were filled with solutions containing considerable amounts of sodium chloride, and saturated with respect to gypsum. The contents of the flasks were evaporated to dryness in platinum dishes on the steam bath; the residues were then washed back into the 100 cubic centimeter measuring flasks which were filled to mark, stoppered, and set aside. From time to time these flasks were vigorously shaken. In one case the solution had been frequently stirred while evaporating on the water bath, and the gypsum crystals which separated were very small. In this case about eight days were required for re-solution to be complete; in the two other cases about sixteen and twenty-two days, respectively, were required, but in all three cases the re-solution was complete in the course of time. It thus appeared that the formation of a different hydrate above 80° was a gratuitous assumption; the more probable explanation of the facts observed is that the rate of solution of gypsum crystals is very slow, even when large amounts of sodium chloride are present.²

Since the experiments just described were made, a paper by van't Hoff and Armstrong³ has been published, from which it appears that the transition point for the two solid hydrates, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, is 101.45° when in contact with a solution of sodium chloride of considerable concentration. With certain other substances, however, this transition temperature is much lower. For example, these investigators found it convenient to prepare the hydrate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, by keeping gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, in contact with concentrated nitric acid at 40° for some time. It might be supposed that this transition takes place at this lower temperature on account of the strong affinity of the nitric acid for water. The results of Vater⁴ rather tend to confirm this view. He found that from saturated solutions of sodium chloride at all ordinary temperatures calcium sulphate separated in the form of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. This hydrate also separated from solutions containing as much as 3 per cent of magnesium chloride; but from saturated solutions of mag-

¹Pogg. Ann., 93, 606.

²Since this work was done, Ostwald, Zeit. für physk. Chem., 34, 495 (1900) has suggested that a substance may have different solubilities, depending upon the size of the particles of the solid in contact with its solution. It is believed, however, that it has been amply demonstrated that in these gypsum solutions that final equilibrium conditions will be the same, and it is the rate of solution which has been the disturbing factor hitherto in their study.

³Sitzungsber. K. Preuss. Akad. Wiss., 28, 559–576 (1900). See also Zunino, Gazz. Chim. Ital., 30, I, 333 (1900).

⁴Sitzungsber. K. Preuss. Akad. Wiss., 28, 269–294 (1900).

nesium chloride gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, separated below 40° , and the hydrate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, above 40° . Magnesium chloride has a strong tendency to crystallize under such conditions as the hexahydrate; that is to say, shows a strong affinity for water. From these facts it would seem that gypsum is not a stable hydrate above 40° in the presence of other substances which are strongly deliquescent, but that in the presence of a neutral substance like sodium chloride, which does not form a hydrate either in the solid or liquid phase, it is stable up to a temperature of 101.45°C .

It will be recalled that the maximum solubility of calcium sulphate in water is at about 40°C . (more exactly, 37.5°), and the idea suggests itself that perhaps this is the true transition point; the supposed solubility curve for gypsum from 0° to 100° being in reality two solubility curves—one for the dihydrate and the other for the hemihydrate—intersecting at 37.5° , both being so flat they run into each other as though but one curve. But this view is negatived by the fact that the transition does not take place in contact with sodium chloride solution until a temperature of 101.45° ; and, as will presently be shown, it does not apparently take place at all in a perfectly indifferent medium at any temperature below that sufficient to drive out all the water from the substance. Further, the transition of gypsum to the hemihydrate when in contact with pure water above 40° has not yet been observed.

The statements of van't Hoff and Armstrong and of Vater were confirmed by experiments in which some cleavage pieces of a very fine gypsum crystal were put into the various solutions at the temperatures stated. When transformation to the hemihydrate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, took place, the surface of the gypsum soon became very white and opaque and the surface roughened, but after standing some time, if dropped into water, the opacity disappeared and the substance gradually became perfectly clear and transparent again. This transformation from one hydrate to another could be very beautifully and readily followed when the cleavage piece was in contact with sodium chloride solutions, for the changes were then fairly rapid. It seemed worth while to see if the transition temperature would be the same when the hydrate was in contact with other presumably neutral substances. Therefore a clear transparent cleavage piece of gypsum crystal was dropped into a test tube containing melted paraffin and the temperature gradually raised by immersing in a water bath to which sodium chloride was added from time to time to raise the boiling temperature. No transition to the hemihydrate appeared when the temperature reached 101.50°C . The temperature was then raised to 104° and kept constant for about six hours. No formation of the hemihydrate could be observed, and the temperature was then gradually raised to 115° without any change in the gypsum being apparent. The test tube containing the paraffin and gypsum was then withdrawn from the bath

and quickly heated to about 145° C. over a bunsen lamp. At this temperature the crystal rapidly lost water, crumbled to pieces, and the residue appeared to be the anhydrous salt, CaSO_4 , although a more thorough analytical examination would be desirable before making this statement positively. From these facts it is apparent that the equilibrium between the hydrates of calcium sulphate needs further study. But the work was stopped at this point, as further investigation in this direction was scarcely pertinent to the subject of this paper.

RATE OF SOLUTION OF GYPSUM.

In order to get some idea as to how long it would be necessary to allow a solution of sodium chloride to stand in contact with gypsum in order to become saturated with respect to the latter, a large quantity of a solution containing 79.08 grams sodium chloride per liter was prepared. To this solution was added about a gram and a half of gypsum, prepared by pulverizing some selected crystals in an agate mortar. The whole was shaken vigorously for a few minutes. From time to time measured quantities were filtered off, and the amount of calcium sulphate dissolved was estimated by precipitation of the sulphate as barium sulphate. After each filtration the solution with the suspended gypsum was vigorously shaken and set aside until required for the next filtration. The data obtained are given in the following table, the first time reading indicating when the powdered gypsum was added to the sodium chloride solution:

TABLE XIV.—*Rate of solution of gypsum in solution of sodium chloride.*

Time.	CaSO_4 per liter dissolved.
	Grams.
10.00 a. m.	0.00
10.17 a. m.	5.19
10.53 a. m.	5.51
11.17 a. m.	5.76
11.48 a. m.	6.02
1.04 p. m.	6.04

At 9.30 a. m. the following forenoon the amount of gypsum dissolved had not sensibly increased, and it was not until nearly three days after the beginning of the experiment that the solution could fairly be considered as saturated, containing 7.45 grams of calcium sulphate per liter. Unfortunately, no attempt was made to keep the temperature of the solution constant, nor were the temperatures recorded during this experiment. As a matter of fact, the temperature of the room became quite low during the nights, and this probably checked somewhat the rate of solution.

The subject is one of great importance in analytical operations. A great deal of trouble has been met in concentrating or evaporating to dryness "alkali" waters containing sulphates and lime salts and then attempting to redissolve the residue for purposes of analysis. It is

frequently desirable for certain work in this Division to prepare artificially, aqueous solutions of salt mixtures. These mixtures are based on the results of chemical analyses of natural water and solutions of soil components, and often these analyses, expressed in the conventional way, show very considerable amounts of calcium sulphate. It has frequently happened that these mixtures could not be made to dissolve in a reasonable time, and the undissolved residue has generally proved to be calcium sulphate when examined chemically. This has sometimes resulted in grave doubt being thrown upon the analyses, besides introducing other annoying features. From what has just been said, however, a way of at least mitigating the difficulty suggests itself; that is, to recalculate the analyses and components of the salt mixture in such a way that the calcium ions and sulphions may each be introduced in the form of more soluble salts. Unfortunately the difficulty can not always be fully met, even when the components are dissolved separately and the solutions brought together, for local supersaturation sometimes causes a separation of fine gypsum crystals which redissolve but very slowly. Nevertheless, this procedure is advised wherever the conditions of the work will permit.

SOLUBILITY OF GYPSUM IN PURE WATER.

The solubility of calcium sulphate in pure water has been frequently determined, but the published results are very conflicting. To account for the discrepancies most astonishing statements as to the supersaturation and under saturation, etc., are recorded. The real cause of the difficulty seems to have been the very slow rate of solution, the time necessary for the obtaining of final equilibrium between the solid solute and solution being relatively very long. For the sake of a comparison, some of the principal determinations at temperatures near that at which we worked are presented in Table XV.

TABLE XV.—*Solubility of gypsum in pure water.*

Authorities.	Temperature.	Parts water required to dissolve 1 part calcium sulphate.	Parts water required to dissolve 1 part gypsum.
Marignac	{ ° C. 24	479	378
Ann. Chim. et Phys. (5), 1, 274 (1874).	{ 18	488	386
Poggiale	20	415	-----
Ann. Chim. et Phys. (3), 8, 469 (1843).	21.2	-----	419
Church	22	538	426
Jahresbuch über die Fortschritte, etc., p. 192 (1867).	{ 20	-----	371
Cozza	{ 25	-----	365
Gazzetta Chim. Italiana, p. 135 (1873).	{ 20	-----	371
Droeze	{ 25	-----	365
Ber. deutsch. chem. Gesellschaft, 10, 330 (1877).	{ 22.5	480	-----
Goldammer	18	483	383
Chem. Centralblatt, p. 708 (1888).	26	469	372
Kohlrausch and Rose	-----	-----	-----
Zeitschrift für phys. Chem., 12, 241 (1893).	-----	-----	-----
From data of this paper	-----	-----	-----

a Calculated from the published data. Under the circumstances the agreement with Marignac's results is remarkable.

The first column gives the authority, with reference; the second column, the temperature at which the solubility was determined; the third column, the parts of water required to dissolve one part of calcium sulphate, calculated on the basis of the anhydrous salt; and the fourth column, the corresponding calculation on the basis of the dihydrate.

Droeze seems to have given much attention to this solubility determination and, besides making experimental investigations himself, has given a critical review of the work of his predecessors in this direction. He objects to Poggiale's figures, that they were probably obtained by working with a supersaturated solution. That this could have been possible seems absurd, and it is much more probable that Poggiale did some very bad analytical work, for his results are phenomenally high. Again, Droeze objects to Church's results, that they were obtained from unsaturated solutions. The reasons for this conclusion are vague, but we are inclined to hold the conclusion itself to be correct, for Droeze's results agree fairly well with those of Marignac, Goldammer, and Kohlrausch and Rose, while the figures of Poggiale, Church, and Cozza show wide variations.

The solubility, as determined from the data presented in this paper, is somewhat greater than is indicated by the figures of the majority of the investigators cited, but not quite as great as found by Droeze. No special care was observed in obtaining this determination, for at the time the experiment was made it was regarded only as an incident in the gathering of data for the solubility curve and not as a point under special investigation. Nevertheless, it is believed that the value as given here is approximately correct, for it is not easy to see in what respect the details of the experimental determination could be bettered. There can be little or no doubt that final equilibrium between the solid salt and the solution had been reached. The analytical operations involved were carefully performed and the calculations were based on the actual weights of the solvent, as well as the solute found to be present.

THEORETICAL DISCUSSION.

The effect of one electrolytic upon another in aqueous solution can be accounted for by the electrolytic dissociation theory, at least qualitatively. Attempts have not been wanting to formulate a quantitative expression for the phenomena observed. Nernst¹ and Noyes², with his pupils, in particular have attacked the problem with marked success by applying the *mass law* of Guldberg and Waage to the par-

¹Zeits. für phys. chem., 4, 372 (1889): Theoretical Chemistry (Palmer), p. 406.

²Zeits. für phys. chem., 6, 241 (1890); 9, 603 (1892); 16, 125 (1899); 26, 152 (1898); 27, 267 (1898); Jour. Am. Chem. Soc., 19, 930 (1898); 20, 194, 742, 751 (1898); 21, 217, 511 (1899).

ticular types of equilibria between electrolytes and their resulting ions which may be presented.

For the case where a pair of binary electrolytes react with the formation of another pair of binary electrolytes and four ions the theory involves the solutions of nine simultaneous equations containing nine variables. For particular cases eight of these variables are determined by various means, and in consequence there is obtained one equation in one unknown quantity, but it is of a high order and involves a very large number of terms. In all the cases so far studied they were so selected that certain restrictions were imposed, arising from the nature of the particular cases themselves, which greatly facilitated their study. Certain special assumptions could be made by which the algebraic expression of the relation between the quantities involved would be very much simplified.

In the case which is the subject of this paper no such assumptions appear justified. In the first place, the concentrations involved are far from what may fairly be considered dilute. All the substances involved in the metathesis $\text{CaSO}_4 + \text{NaCl} \rightleftharpoons \text{CaCl}_2 + \text{Na}_2\text{SO}_4$ are *strong* electrolytes to which the Ostwald dilution law does not apply—that is to say, to which the mass law is *not* applicable as a statement of the equilibria between the quantities of dissociated ions and undissociated salt through any range of concentrations. The ionization constants, which appear in the equations to which reference has just been made, can not be obtained, therefore, in any way which we can at present see. In the case of the calcium chloride and the sodium sulphate supposed to be in the solution there did not appear to be any practicable way to decide in how far the dissociation would take place as for a di-ionic electrolyte or how far as for a tri-ionic electrolyte, with a consequent modification of the theoretical statements. These considerations have finally caused the abandonment of any attempt to make a comparison between theoretically computed results and those actually found, and, in the present state of our knowledge, the results can be presented only as empirical determinations in the trust that in time they may find use in helping to develop a more comprehensive and satisfactory theory for solutions. An approximate idea of the composition of the solution may be obtained, however, from the following considerations:

Since calcium sulphate in the form of gypsum was always present in the solid phase in contact with the solutions, Nernst's¹ theorem will apply to this case, and it may be assumed that the amount of calcium sulphate dissolved but undissociated will be the same for every point on the curve—that is to say, that no matter what the concentration of the solution may be with respect to sodium chloride, the amount of calcium sulphate *as such* which it will dissolve is always the same.

¹Theoretical Chemistry, p. 446. See also Report 64, Division of Soils, p. 148 (1900).

If it be assumed that the mass law holds with reasonable accuracy for the conditions of equilibrium between the undissociated calcium sulphate and its ions, Ca^{+} and $\overline{\text{SO}_4}$, it follows further that the number of calcium ions and sulphions is a constant for every concentration of the solution with respect to the sodium chloride. The quantitative measurements for these quantities are readily made from the conductivity of a saturated solution of calcium sulphate in pure water.

In fig. 6 these facts are illustrated graphically. Simply for convenience, the diagram is somewhat distorted. Suppose AO to indicate the solubility of calcium sulphate in pure water; BO to indicate the amount of the salt undissociated; AB to indicate the amount of calcium ions or sulphions present. If then the amount of calcium, for instance, in the solution be determined for any point C on the curve and indicated by CF, the amount indicated by EF (=BO) will be present in the form of calcium sulphate undissociated; the amount indicated by DE (=AB) will be present in the form of calcium ions;

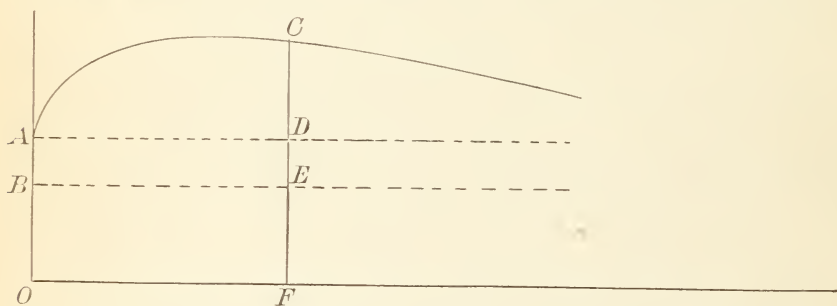


FIG. 6.—Diagram illustrating concentrations of undissociated salts and corresponding ions in solutions of salt mixtures.

and a necessary consequence is that the amount indicated by CD must be present in the form of calcium chloride undissociated.

In a strictly analogous way the amount of undissociated sodium sulphate present in the solution can be determined. For the complete solution of the problem the amounts of chlorine and sodium as ions and the salt sodium chloride undissociated are required. The difficulties in the way of obtaining these quantities are too great, however, for a practical solution at present.

There does not appear to be any rational explanation for the appearance of the maximum point on the solubility curve. One would naturally expect the solubility of the gypsum to continually increase as the concentration with respect to sodium chloride increases. Noyes¹ has brought forward some evidence to show that as the concentration increases with respect to chlorides of the alkali earth metals, there is a formation of complex ions, for example CaCl_3 or CaCl_4 . The evidence he obtained was rather against the assumption that the

¹ Phys. Rev., 12, 14 (1901), Jour. Am. Chem. Soc. 23, 37 (1901); Zeit. für phys. Chem., 36, 61 (1901).

sulphates of the alkali metals would dissociate in any but a normal way, as trionic electrolytes; but he worked with quite dilute solutions (up to a tenth molar), and it does not follow that complex ions would not be found in solutions of the concentrations considered in this paper. It is difficult to see how the formation of such complex ions could affect the gypsum in contact with the solution, otherwise than to increase its solubility; and the fact that the solubility actually decreases beyond the maximum point is, as far as it goes, rather to be considered as evidence against the formation of the complex ions. The same thing might be said as to the suggestion that all electrolytes are considerably hydrolyzed at high concentrations.

It seems more probable that the phenomenon is connected with the condensation of the solvent and the effect of such condensation upon the solution tensions of the various electrolytes, and it is earnestly to be desired that some one with time and opportunities undertake an investigation of this subject.

APPLICATION OF RESULTS.

That such data as have been obtained in this investigation will prove of great value in the study of "alkali" problems can scarcely be open to doubt. It is true, as has been pointed out above, that we seldom have to deal with a reaction between but a pair of electrolytes; but it has been clearly brought out in the study of the soils of the valley of the Pecos River, New Mexico, that the more important components of the "alkali" there found are calcium sulphate and sodium chloride. There are large deposits of gypsum scattered throughout this area, and by far the most abundant solute in the waters which come into contact with this gypsum is sodium chloride. The study of the resulting waters, from irrigation, seepage, etc., is largely a study of the equilibrium between these two electrolytes in the solution; to a lesser or greater extent complicated by the presence of other salts, by physical phenomena, etc. Knowing the nature of the water in any particular instance and the soils with which it will come in contact, a much clearer idea of the resulting effects can be prophesied in the light of the data presented in this paper. Much more is yet to be learned, however, before it will be possible to confidently predicate *a priori* much about any particular solution in contact with a soil; for the conditions are exceedingly complex and the many factors entering the problem are very difficult to recognize and follow. For example, it can be readily seen from these solubility curves, how much calcium chloride can be formed in the soils of the Pecos Valley;¹ but it is not so evident why this material should accumulate in a greatly preponderating amount in certain spots, keeping the earth moist in the driest weather and giving it a darker color than the sur-

¹ Report 64, U.S. Department of Agriculture. A Soil Survey of Pecos Valley. By Thos. H. Means and F. D. Gardner.

rounding drier soil to such an extent as to cause such spots to be locally designated as "black alkali." One surface scraping analyzed in this laboratory¹ for its water soluble constituents gave the following results:

CaSO ₄	13.39
CaCl ₂	40.58
MgCl ₂	18.20
NaCl.....	27.83

from which it appears that at least 40 per cent of the soluble matter must have been calcium chloride. Many similar examples from other areas might be quoted. A sample sent to this laboratory from near Salt Lake City showed even more astonishing amounts of calcium chloride. Unfortunately, the quantitative figures can not be presented, but at least 60 per cent of the total sample must have been calcium chloride.² Before such phenomena can be fully understood, much fuller knowledge of the rates of diffusion of the various salts and of the absorption power of the soil grains, etc., must be had. The study of the mutual influence of the electrolytes on their solubility is but the necessary first step in solving the problem presented to us.

The transportation of calcium salts and sulphates through the soil is much more clearly understood in the light of the facts brought out in this paper, and the fact that beyond a certain point gypsum is precipitated from the solution with an increase of sodium chloride in the solution has given a clue as to the formation of gypsum layers in the soil in some of the arid regions. A clearer insight has been obtained as to the formation of alkali and alkali crusts, and this has led to a comprehensive classification of alkali lands, which is described elsewhere.³

It is believed, moreover, that the data here presented may find further usefulness in some technical operations, as in the working up of brines, in the preparation of salt, and in the removal of boiler scales, etc. These subjects can only be mentioned, however, in this connection.

For assistance in carrying out the experimental and analytical details of the work described in this paper, the author wishes to

¹ Loc. cit., p. 74, soil sample 4058.

² This material was leached with distilled water and filtered. The filtrate, after concentrating, was allowed to stand in a desiccator over sulphuric acid, with the result that an astonishingly large amount of the salt calcium chloride (presumably the hexa-hydrate) separated in large, well-characterized crystals. There were also present crystals of sodium chloride and some little strontium chloride, both these latter salts in greatly lesser amounts than the calcium chloride. A complete identification of these products was made by Mr. Wirt Tassin, of the United States National Museum.

³ Bulletin 17, Division of Soils.

record his sincere acknowledgments to Messrs. Frank D. Gardner and Atherton Seidell of this Division.

SUMMARY.

Some of the points brought out in the foregoing pages to which attention is especially directed may be stated as follows:

(1) Below 37.5° C. the solubility curves for gypsum in aqueous solutions of sodium chloride show a maximum point. Above this temperature the existence of maximum points is doubtful.

(2) At 23° C. this maximum solubility takes place in a solution containing from 135 to 140 grams sodium chloride per liter.

(3) The solubility of gypsum at 23° in a solution containing 135 grams of sodium chloride per liter is about 9.3 grams per liter. This is equivalent to about 7.5 grams of anhydrous calcium sulphate per liter.

(4) The solubility of gypsum in solutions containing less than 140 grams of sodium chloride per liter is very little affected by change of temperature.

(5) Maximum points in the solubility curve still persist, even if the solubilities be calculated on the basis of the weight of solvent present rather than the volume of the solution.

(6) A condensation of the water as solvent takes place when gypsum and sodium chloride are brought into solution.

(7) The rate of solution of gypsum is very slow, and at ordinary temperatures the time required for equilibrium to be brought about is often great. This fact accounts for the apparent insolubility of gypsum crystals in that volume of solution from which they were originally obtained.

(8) The transition temperature at which the dihydrate and hemihydrate of calcium sulphate are in equilibrium appears to be dependent upon the nature of the substance or substances in the solution with which they are in contact.

(9) At 26° the solubility of gypsum is about 1 part in 372 parts of pure water.

(10) The specific gravity of a saturated solution of gypsum in pure water is 1.0026 at 26° C., and 1.0031 at 31° .

(11) The application of the mass law, as formulated by Guldberg and Waage, to the phenomena of electrolytic dissociation fails to account for the observations here recorded.

(12) The existence of a maximum point on the solubility curve is not accounted for by the hypothesis of the existence of complex ions in the solution. It is probably connected with the condensation of the solvent in aqueous solutions of electrolytes.

(13) The data presented furnishes, in part at least, an explanation of certain phenomena observed in studying alkali soils, and possible applications in technical processes are suggested.

SOLUBILITY OF GYPSUM IN AQUEOUS SOLUTIONS OF CERTAIN ELECTROLYTES.

By FRANK K. CAMERON and ATHERTON SEIDELL.

INTRODUCTION.

The results obtained in the study of the solubility of gypsum in aqueous solutions of sodium chloride were of such a character as to make it appear desirable to obtain data for other solutions of a similar kind. The work was therefore continued and a description of the investigation is here recorded. The choice of the electrolytes was governed mainly by the desire to throw light upon certain problems arising in the study of alkali lands by the field parties of this Division, which problems need not be more particularly described at this point. The solubility of gypsum was therefore determined in solutions of magnesium chloride, calcium chloride, sodium sulphate, and in solutions of sodium chloride when calcium carbonate in the solid phase was also in contact with the solution.

All these determinations were made at temperatures from 23° C. to 26° C. The temperature of the laboratory held quite constantly within these limits and, as slight changes of temperature were found to affect the solubility of gypsum in these solutions but very little, it was not deemed necessary to use a constant temperature bath.

It is desirable for some reasons, both scientific and technical, that determinations should be made at other temperatures, especially above 40° C.; but the exigencies of the public service hardly seemed to warrant them being made at this time.

Instead of gypsum, precipitated calcium sulphate, obtained from Baker and Adamson and labeled C. P., was used in these experiments. It was found by examination of a few solutions that, as was the case in sodium chloride solutions described in the preceding paper, the same results were obtained with gypsum and with precipitated calcium sulphate; but that the solutions came to equilibrium more rapidly when the latter was used. The other salts used in the investigation were chemically pure materials obtained from the same firm.

The general method of procedure was the same in all cases. A series of solutions of various concentrations with respect to the readily soluble salt was prepared, and enough calcium sulphate added to insure an excess of this substance in the solid phase. The solutions were then set aside for periods of from one to six weeks, with occasional vigorous shaking.

The solutions were generally of about 700 c. c. volume and were contained in liter Florence flasks fitted with rubber stoppers, to prevent

evaporation of the solvent. When ready for analysis, they were allowed to settle, and appropriate portions of the clear supernatant solutions were drawn off with a pipette, and whenever this procedure seemed advisable they were filtered. The analytical operations were conducted according to the conventional methods and call for no special comment. The amount of calcium sulphate which had dissolved was calculated from the amount of sulphions found in the solution. The results obtained are presented graphically in fig. 7; the ordinates represent grams per liter of calcium sulphate, and the abscissas represent grams per liter of the more soluble salt used.

For some reasons it seemed more advisable to give the results in terms of calcium sulphate found in the solution rather than in amounts of gypsum found to be soluble. These latter can always be readily

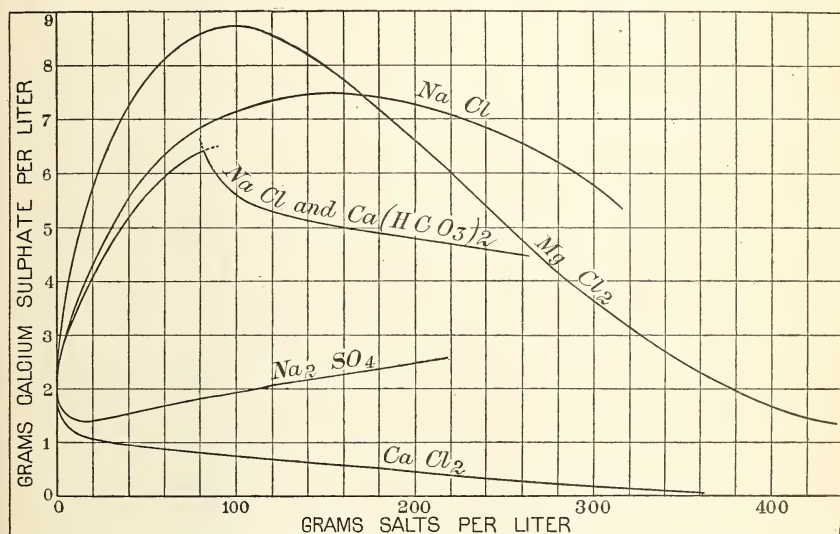


FIG. 7.—Diagram showing solubility curves for calcium sulphate in solution of other salts. Results given in terms of grams per liter.

obtained by multiplying the given results by the factor 1.2647. In fig. 8 the solubility curves are given in terms of the number of reacting weights found in the solution.

Although the temperature was not quite the same for these different series of determinations, in all these series it was found that such small differences of temperature as are involved here have such a small influence on the solubility of the calcium sulphate that these curves may fairly be considered as entirely comparable.

SOLUBILITY OF CALCIUM SULPHATE IN MAGNESIUM CHLORIDE SOLUTIONS.

It was found that the curves illustrating this case showed unusually well-marked maximum points. Therefore it was deemed advisable to determine the curve with reference to a constant weight of

the solvent water as well as to a constant volume of the solution. The data obtained at 26° C. are given in the accompanying table, which is self-explanatory. The results, referred to a constant volume of solution, are presented graphically in figs. 7 and 8.

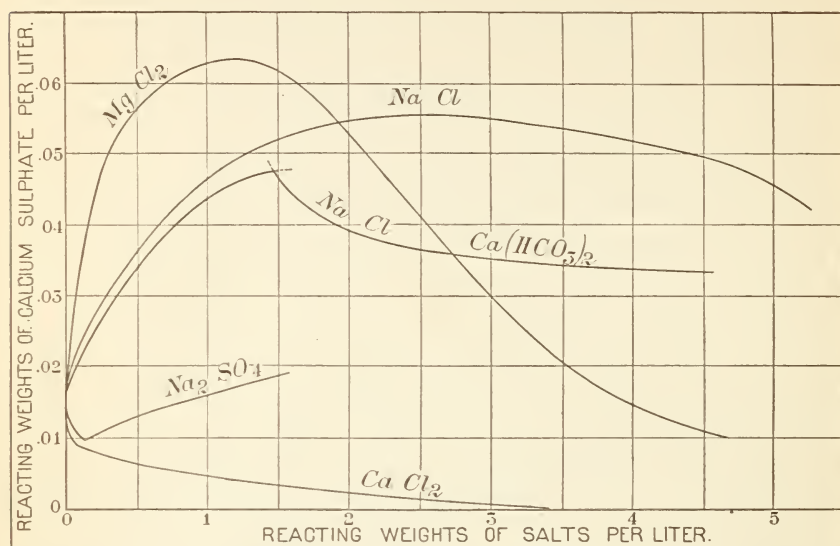


FIG. 8.—Diagram showing the solubility curves for calcium phosphate in solutions of other salts. Results given in terms of reacting weight per liter.

TABLE XVI.—Solubility of calcium sulphate in aqueous solutions of magnesium chloride at 26° C.

H ₂ O grams per liter).	CaSO ₄ .		MgCl ₂ .	
	Grams per liter.	R. Wts. per liter.	Grams per liter.	R. Wts. per liter.
997.924	2.082	0.0154	0.000	0.0000
996.520	4.258	.0315	8.501	.0003
994.489	5.692	.0421	19.175	.2030
989.143	7.588	.0561	46.640	.4938
972.218	8.622	.0638	121.381	1.2850
949.950	6.567	.0486	206.985	2.1912
908.678	2.774	.0205	336.986	3.5674
878.588	1.385	.0102	441.128	4.6699

CaSO ₄ .		MgCl ₂ .	
Grams per 1,000 grams of water.	R. Wts. per 1,000 grams of water.	Grams per 1,000 grams of water.	R. Wts. per 1,000 grams of water.
2.086	0.0154	0.000	0.0000
4.273	.0316	8.531	.0003
5.724	.0423	19.860	.2102
7.674	.0568	47.170	.4993
8.867	.0656	124.800	1.3212
6.913	.0511	217.900	2.3068
3.553	.0263	370.900	3.9265
1.577	.0116	502.000	5.3144

By interpolation on the curves it appears that the maximum solubility for calcium sulphate is about 8.8 grams per liter in a solution containing about 105 grams per liter of magnesium chloride. In this solution, therefore, there is more than four times as much calcium sulphate as in a saturated solution of this substance alone. Calculated as gypsum, this maximum solubility is 11.129 grams per liter, or 4.23 times as much as is soluble in pure water. Beyond the maximum point the solubility of the calcium sulphate decreases quite rapidly as the concentration with respect to magnesium chloride increases, this decreasing solubility being much more rapid than in the corresponding curve for the solubility of gypsum in sodium chloride solutions. This decrease in solubility continues until in a solution containing about 370 grams magnesium chloride per liter the solubility of gypsum is the same as in pure water. Therefore, even in the presence of this salt, which does not yield a common ion, the solubility of gypsum is less at high concentrations than in pure water.

The curve plotted from the data obtained on the basis—grams of salt per 1,000 grams of the solvent is of the same general nature as the curve plotted on the basis of a constant volume of solution, and shows about equally well the character of the phenomena involved. The former lies slightly above the latter, and it does not seem worth while to chart it here. Attention is called to it for it also shows, in a most striking way, the real existence of a maximum point on the solubility curve. It would seem that this pair of electrolytes may be particularly well adapted to a further study along the general lines indicated by the investigation here described.

An inspection of a number of analyses of the water-soluble components of soils in arid regions confirms the results indicated above, in that when the percentage of magnesium and chlorides is large there is evidently a large increase in the solubility of the gypsum in the soils. The explanation of such a conclusion could hardly have been drawn from the inspection of the analyses alone, and, in fact, the relatively large amount of calcium stated in these analyses has sometimes caused grave doubts as to their accuracy. Another point of interest in the curves for this pair of electrolytes is the wavy character for the higher concentrations with respect to magnesium chloride. To what this may be due can not be said at present, but it shows that in all probability complex molecular or ionic changes must take place in the solution at these higher concentrations and that the subject is much in need of further investigation.

By referring to fig. 8 it will be observed that the maximum point on the curve for magnesium chloride occurs at about half the concentration that it does on the curve for sodium chloride; that is, at about the same concentration for chlorine in the two cases, since a reacting weight of magnesium chloride contains twice as much chlorine as does a reacting weight of sodium chloride. But the total

amount of calcium sulphate is different in the two cases, showing that magnesium and sodium have markedly different properties, at least in degree, under such circumstances.

SOLUBILITY OF CALCIUM SULPHATE IN CALCIUM CHLORIDE SOLUTIONS.

In the preparation of the calcium chloride solutions for this series of experiments it was found that the solutions were more or less turbid, due to undissolved calcium hydrate originally present in the supposed chemically pure calcium chloride used. A few drops of methyl orange solution were therefore added in each case, and then hydrochloric acid, until the indicator showed the solutions to be neutral. The solutions became perfectly clear and free from suspended matter. The calcium sulphate was then introduced and the usual procedure followed.

In this case the two salts will yield a common calcium ion, and in consequence the solubility of the calcium sulphate will be much decreased by the presence of the calcium chloride. This is shown by the accompanying table of results, obtained on a series of experiments made at 25°C. It is even more strikingly brought out by the graphical representation of the results in figs. 7 and 8. The observations on this pair of electrolytes made by Tilden and Shenstone¹ and by Lunge² agree in general with the results given here.

TABLE XVII.—*Solubility of calcium sulphate in aqueous solutions of calcium chloride at 25°C.*

CaSO ₄ .		CaCl ₂ .	
Grams per liter.	R. Wts. per liter.	Grams per liter.	R. Wts. per liter.
2.056	0.01521	0.000	0.00000
1.244	.00921	7.489	.06801
1.181	.00874	11.959	.10860
1.096	.00811	25.770	.23401
1.080	.00799	32.045	.29100
1.016	.00752	51.530	.46794
.841	.00622	97.023	.88106
.465	.00344	192.705	1.74996
.203	.00150	280.303	2.54543
.032	.00024	367.850	3.34045

The solubility of the calcium sulphate decreases very rapidly as the concentration with respect to calcium chloride increases, until a concentration of about 20 grams per liter of this latter salt is reached. From this point the solubility of the calcium sulphate decreases more slowly but steadily, until by extrapolation on the curve it would seem that the solution containing 375 grams per liter of calcium chloride would dissolve practically no calcium sulphate.

Just why there should be so marked a change in the solubility of the calcium sulphate in a solution at a concentration of about 2 per cent

¹ Proc. Roy. Soc., 38, 335 (1885).

² Jour. Soc. Chem. Ind., 4. 31 (1885).

calcium chloride does not admit of explanation as yet. It is possible that at concentrations above this the calcium chloride may partially dissociate in such a way as to form complex ions containing both calcium and chlorine¹ and thus diminish the proportional effect of calcium as ions in the solution, forcing back the dissociation of the calcium chloride and consequently the retarding effect upon the solubility of the calcium sulphate. It seems probable, however, that the density of the solvent itself may have an important rôle in this connection.

THE SOLUBILITY OF CALCIUM SULPHATE IN SODIUM SULPHATE SOLUTIONS.

In this case it is to be expected that the two electrolytes would yield the common sulph-ion, therefore the solubility of the gypsum should decrease as the concentration with respect to sodium sulphate increases. Such was found to be the case up to a concentration of about 17.5 grams per liter of sodium sulphate, when the solubility of the calcium sulphate was about 1.38 grams per liter, or 1.745 grams per liter of gypsum. At this point, as the concentration with respect to sodium sulphate increases, there is a sudden change in the direction of the curve and the solubility of the calcium sulphate steadily increases until, in a liter of solution containing 230 grams of sodium sulphate, there will be dissolved 2.5 grams of calcium sulphate—a quantity markedly larger than will be dissolved by pure water. The data obtained for this pair of electrolytes are given in the following table:

TABLE XVIII.—*Solubility of calcium sulphate in aqueous solutions of sodium sulphate at 22° C.*

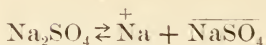
CaSO ₄		Na ₂ SO ₄	
Grams per liter.	R. Wts. per liter.	Grams per liter.	R. Wts. per liter.
2.084	0.0154	0.000	0.0000
1.583	.0117	2.771	.0196
1.433	.0106	13.820	.0979
1.408	.0104	16.360	.1159
1.569	.0116	39.310	.2786
1.841	.0136	77.320	.5480
2.185	.0162	133.000	.9425
2.414	.0178	193.800	1.3734
α 2.578	α .0190	α 222.580	α 1.5773

α Both calcium sulphate and sodium sulphate in the solid phase were in contact with the solution.

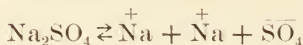
Apparently we have to deal with two solubility curves which intersect at the minimum point. Possibly, at concentrations with respect to sodium sulphate greater than that at the minimum point the

¹ Noyes, Physical Rev., **12**, 14, (1901); Jour. Am. Chem. Soc., **23**, 37, (1901); Zeit. für phys. Chem., **36**, 61, (1901).

dissociation of the sodium sulphate takes place in part according to the scheme:



rather than entirely as indicated thus:



If this be so, it is tantamount to introducing a substance into the solution which does not yield a common ion with calcium sulphate, and which therefore may be expected to increase the solubility of the latter. We thus have the sodium sulphate exerting two effects on the solubility of the calcium sulphate, depending on the way in which it dissociates. These two effects are opposite in direction, and in consequence the resulting effect will be dependent on the relative amounts of the dissociation in the two different ways, which is dependent in turn upon the concentration of the solution with respect to the sodium sulphate itself.

From this point of view one would expect the existence in the solution of a double salt, possibly of the composition $\text{Ca}(\text{NaSO}_4)_2$. Such a salt is probably the mineral glauberite found in nature, and in fact believed to be a common constituent of some alkali soils. Fritzsche¹ describes a hydrated double sulphate ($\text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$) obtained by heating gypsum with a small amount of water and a large excess of Glauber salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). The substance was a well characterized one, crystallizing in fine needles, which, on heating, quickly lost the water it contained, yielding the anhydrous double salt. It was expected, therefore, that this salt, or its hydrate, might be obtained by evaporating solutions of sodium sulphate saturated with respect to calcium sulphate. Such solutions were prepared and allowed to evaporate spontaneously at the room temperature. No evidence of the presence of the double salt, however, could be detected in the residue after evaporation of the water. It should be remembered that in those areas where this double calcium sulphate has been observed in nature, the ground temperatures are frequently very high and the equilibrium conditions for the solution may well be very different from those obtaining at 25° C.

An experiment was then made to see if the composition of the solid phase would affect the composition of a solution in contact with both salts in the solid phase. Four vessels were prepared. In each was placed 100 c. c. of water and 40 grams of sodium sulphate and 1, 2, 5, and 10 grams of calcium sulphate, respectively, insuring the presence of both salts in the solid phase. The vessels were then placed in a shaking apparatus and shaken constantly for four days. The contents were allowed to settle and the supernatant solutions quickly decanted upon folded filters. Aliquot portions of the filtrates were

¹ Jour. für prakt. Chem., 72, 291 (1857).

analyzed for calcium and sulphates. It was found that the composition of the solid phase apparently did not affect the composition of the solution, practically identical results being obtained in all four analyses. The solution in contact with both salts in the solid phase was found to contain 222.5810 grams per liter of sodium sulphate and 2.5783 grams per liter of calcium sulphate. These results were entirely unlooked for, and can only be explained on the assumption that at the temperature at which the work was done, about 25° C., the solubility of the double salt is greater than the solubility of either Glauber salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) or gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and consequently these salts alone will separate from the solution. It is desirable that some one, with time and opportunity for it, should take this matter up and investigate the system throughout a range of temperature. It is a subject of considerable practical importance in several technical operations, as well as in geological and soil studies.

It follows from these experiments that, considerable amounts of sodium sulphate being in the solution, the solubility of calcium sulphate or gypsum may be relatively great, instead of falling to a very small figure; and the amount of gypsum in contact with the solution in the solid phase will not have any effect in determining the amount that will go into solution at ordinary temperatures, even though sodium sulphate also be present in the solid phase.

SOLUBILITY OF CALCIUM SULPHATE IN AQUEOUS SOLUTIONS OF SODIUM CHLORIDE AND IN THE PRESENCE OF SOLID CALCIUM CARBONATE.

As has been pointed out in another publication of this Division,¹ the characteristic feature of certain areas of alkali lands is the action of sodium chloride in aqueous solution upon gypsum and calcium carbonate simultaneously. It was therefore determined to study the solubility of calcium sulphate in sodium chloride solutions when calcium carbonate in the solid phase was also in contact with the solution. The solubility of this latter salt is dependent upon the partial pressure of the carbon dioxide in the gaseous phase in contact with the solutions. Therefore, air which had been previously washed in dilute sulphuric acid was bubbled through the solutions for fifty-one days, or until they came to equilibrium.² The addition of phenolphthalein to the solution did not show the presence of normal carbonates in any of the solutions. The amounts of bicarbonates found, in the equivalents of calcium hydrogen carbonate dissolved, are given in the accompanying table.

¹ Bulletin No. 17, Division of Soils, 1901.

² It is very probable that these solutions had come to final equilibrium within eighteen days, but the passage of air through them was continued to make certain that such a condition had been reached.

TABLE XIX.—*Solubility of calcium sulphate in aqueous solutions of sodium chloride in contact with solid calcium carbonate.*

CaSO ₄		Ca(HCO ₃) ₂		NaCl	
Grams per liter.	R. Wts. per liter.	Grams per liter.	R. Wts. per liter.	Grams per liter.	R. Wts. per liter.
1.9298	0.0143	0.0603	0.000375	0.000	0.0000
2.7200	.0201	.0724	.000450	3.628	.0625
3.4460	.0255	.0885	.000550	11.490	.1979
5.1560	.0381	.1006	.000625	39.620	.6824
6.4240	.0475	.0603	.000375	79.520	1.3696
5.2720	.0390	.0563	.000350	121.500	2.0665
4.7860	.0354	.0482	.000300	193.800	3.3379
4.4620	.0330	.0402	.000250	267.600	4.6090

The variation in the solubility of the calcium carbonate in the solutions of sodium chloride when gypsum was also present in the solid phase will be discussed in more detail in a following paper. The effect of the presence of the calcium carbonate upon the solubility of the calcium sulphate is most strikingly brought out in the graphic presentation of the results in figs. 7 and 8. From a point representing no sodium chloride in solution up to a concentration for this latter salt of somewhat more than 80 grams per liter, the curve follows very closely the curve representing the solubility of calcium sulphate in the presence of sodium chloride alone. The solubility of calcium sulphate steadily increases with increasing concentration of sodium chloride, but at a somewhat diminishing rate from that which obtains when no calcium carbonate was present. As the amount of sodium chloride increases beyond 80 or 100 grams to the liter, the solubility of the calcium sulphate steadily decreases and apparently follows a new curve, the two curves probably intersecting as charted and not forming a continuous curve with a maximum point, as in the case when there is no calcium carbonate present.

It thus appears that while the solubility of gypsum in solutions of sodium chloride would be but little affected by the presence of calcium carbonate up to 8 or 9 per cent solutions, beyond this point its solubility would be considerably diminished. But in solutions nearly saturated with respect to sodium chloride the gypsum would be about twice as soluble as in pure water, even though calcium carbonate be present.

It is interesting to note that while the solubility of calcium sulphate is only about 2.1 grams per liter in pure water, it reaches a maximum solubility of about 7.5 grams per liter in solution containing 140 grams per liter of sodium chloride. But this solubility would be reduced to about 5 grams per liter if calcium carbonate were present, and in the presence of this latter substance the maximum solubility of calcium sulphate is about 6.35 grams per liter in a solution containing only about 80 to 90 grams per liter of sodium chloride.

SUMMARY.

The data which have been presented in the foregoing pages afford much new information on the solubility of gypsum when this substance is a component of the soil. By reference to fig. 3 it will be seen that up to the tenth normal solution the solubility curves in all cases follow, qualitatively at least, the direction indicated by an application of the mass law to the hypothesis of electrolytic dissociation. This is still true for calcium chloride solutions at high concentrations, but in the other cases here recorded it is not true, and it would have been quite impossible to have predicted the character of these solubility curves *à priori*.

The phenomena which have been described in this paper lend support to the view that ionic complexes are formed in solutions of high concentration. Noyes,¹ in a recent publication, has brought forward evidence to show that such ionic complexes are probable in solutions of the chlorides of the alkaline earths, even at quite high dilutions. The investigations in recent years lend much evidence pro and con to the view that such complexes exist, not only in aqueous solutions, but in other solvents.² Of great interest in this connection is the fact brought out by Walden³ that binary electrolytes in general dissociate much more readily than do ternary or quaternary electrolytes. Since it is to be presumed that ternary electrolytes were present in all the solutions studied in this investigation, it is not so surprising, therefore, that abnormal results were observed at the higher concentrations. It seems most probable that all these facts are dependent upon, or at least causally connected with, the considerable condensation of the solvent which takes place when solutes, especially electrolytes, go into the solution; and that much of interest for the general theory of solutions could be obtained by a systematic investigation from this point of view.

It is obvious that mixtures of as simple composition as those described in this paper are quite rare in the soil solutions, and how far the data here presented will be available in discussing such soil solutions is a pertinent question. It must be said that in all probability no strict application of the figures here given can be made in the study of alkali problems, but nevertheless in a qualitative way they are decidedly helpful. For example, it is probably entirely safe to say that the solubility of gypsum in solutions of soluble chlorides increases up to a concentration of from 10 to 15 per cent, and that beyond this concentration the solubility of the gypsum steadily decreases again. The solubility of gypsum in such solutions is probably but little affected by the presence of soluble sulphates. Even

¹ Phys. Rev. 12, 14 (1901); Jour. Am. Chem. Soc., 23, 37 (1901); Zeit. für phys. Chem., 36, 61 (1901).

² See Jones, Am. Chem. Journ., 25, 232 (1901).

³ Zeit. anorg. Chem., 25, 209 (1900).

more specific conclusions can be drawn, with a great deal of probability, from the known conditions in any given case, but they can be discussed better elsewhere, when these conditions are more specifically under consideration.

The facts here presented are of great value in explaining the solution of gypsum, its transportation in the soil, and its precipitation from the soil solution in the presence of large quantities of other soluble salts. This matter of the transportation of gypsum and the formation of gypsum layers at various depths in the soil has been, up to the present time, one of the most puzzling and inexplicable problems connected with the investigation of alkali lands.

The large amounts of gypsum found soluble in the analysis of the water soluble components of alkali soils have often been the cause of much astonishment. In these analyses it is necessary to treat the soil with considerable amounts of water, either by successive leaching or by allowing the soil to stand in contact with an excess of water and drawing off the supernatant solution; and it may well be that in this procedure solutions of the more soluble salts will be found of just the concentrations best suited for dissolving a maximum amount of gypsum. These facts should receive earnest consideration in the study of such analyses and in the forming of conclusions from them, for it is altogether probable that the proportions of calcium and of SO_4 , which the analyses indicate, are greater than exist in the soil solutions in the ground itself.

It seems probable, from the results of this investigation, that wherever gypsum occurs in the soil there will be a considerable amount of calcium in the soil solution. This is now known to be a matter of great importance from a physiological point of view, enabling the plants to withstand much larger quantities of the more soluble salts than would otherwise be possible. This Division has been cooperating with the Division of Vegetable Physiology and Pathology in some studies along this line, and the results thus far obtained will shortly be presented in another publication.

Calcium sulphate is much more soluble than calcium carbonate, even when there is a considerable amount of carbon dioxide present, and the solubility of the latter salt is thus increased through the formation of the more soluble hydrogen carbonate. It has therefore seemed probable that it would be better in many cases to use the sulphate for liming soils, because in this way more calcium is brought into the ground solution and its ratio to the other bases dissolved is much increased, and because its *active mass* in the solution is greater and its effect upon other soil components is correspondingly increased. On the other hand, it can not have the effect that either the carbonate or hydrate of lime has in counteracting an excess of carbonic or other organic acids in sour soils or in making them slightly alkaline—a condition which appears to be desirable for certain crops. Further—

more, the carbonate and hydrate have certain well-marked effects on the texture of soils, which are sometimes of as much or more importance than the purely chemical results; consequently it seems desirable that the comparative value of these lime salts, or mixtures of them, on soils of various character should receive more attention than has hitherto been given, both in the laboratory and in actual field practice.

The application of soluble mineral fertilizers to the soils of humid areas unquestionably affects the solubility of mineral components of the soils. Such cases are analogous to the gypsum solution, in that a slightly soluble substance is brought into contact with solutions of much more soluble substances. The idea suggests itself that, as with gypsum, possibly the mineral components of the soil may have maximum solubilities, in solutions of the more soluble salts of definite concentrations, far below the limit of solubility with respect to the readily soluble salts. Some work along this line has been undertaken by the Division. The subject is of such importance, and the field of investigation is so wide, that it is earnestly hoped that such work will commend itself to the attention of other investigators.

SOLUBILITY OF CALCIUM CARBONATE IN AQUEOUS SOLUTIONS OF CERTAIN ELECTROLYTES IN EQUILIBRIUM WITH ATMOSPHERIC AIR.

FRANK K. CAMERON and ATHERTON SEIDELL.

INTRODUCTION.

The experiments on the solubility of calcium carbonate were made in a similar manner to those described in the preceding papers. Since the solubility of the carbonates is dependent upon the partial pressure of the carbon dioxide in the gas phase in contact with the solution, the effort was made to bring these solutions to equilibrium with ordinary air. Air was therefore drawn through the flasks containing the

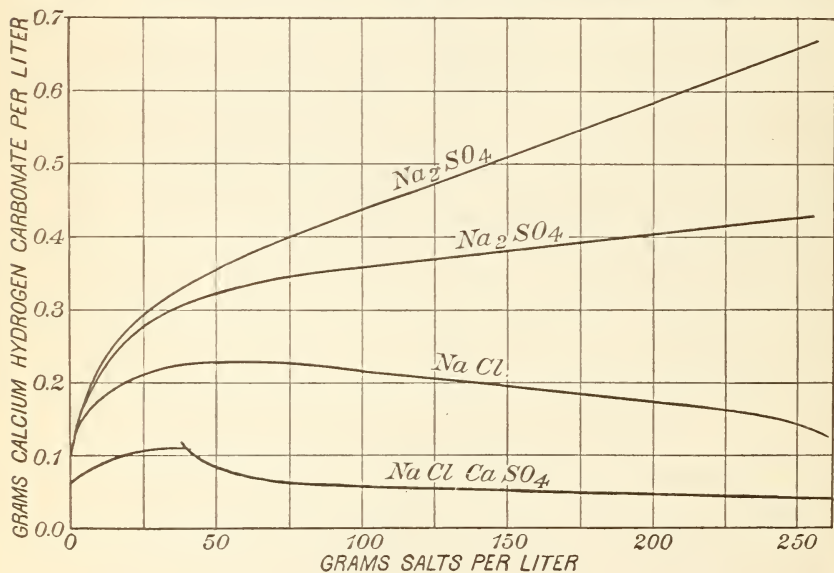


FIG. 9.—Diagram showing solubility curves for calcium bicarbonate in solutions of other salts. Results given in terms of grams per liter.

solutions in contact with the calcium carbonate in the solid phase. The flasks were arranged in series with appropriate rubber and glass tube connections and a continuous stream of air drawn through by an aspirator attached to a hydrant. Before entering the solutions the air was drawn through a dilute solution of sulphuric acid to free it from any traces of ammonia or other impurities in the laboratory atmosphere. Precipitated calcium carbonate was used in order to

take advantage of the large surface exposed by the material in this form, and thus bring the solutions to equilibrium as quickly as possible. All the salts used were obtained from Baker and Adamson, were labeled C. P., and were found to be of a satisfactory degree of purity. As small changes of temperature did not produce any marked effect on the solubility of the calcium carbonate, and as the temperature of the laboratory held quite constant during the period when this work was done, it was not deemed worth while to make use of a constant temperature bath.

Since it was found that the major part of the calcium went into solution as the hydrogen carbonate rather than as the normal carbonate, the calcium dissolved is stated in terms of the hydrogen carbonate. Of course the statements and charts in terms of reacting weights would be the same for either the normal or hydrogen carbonate.

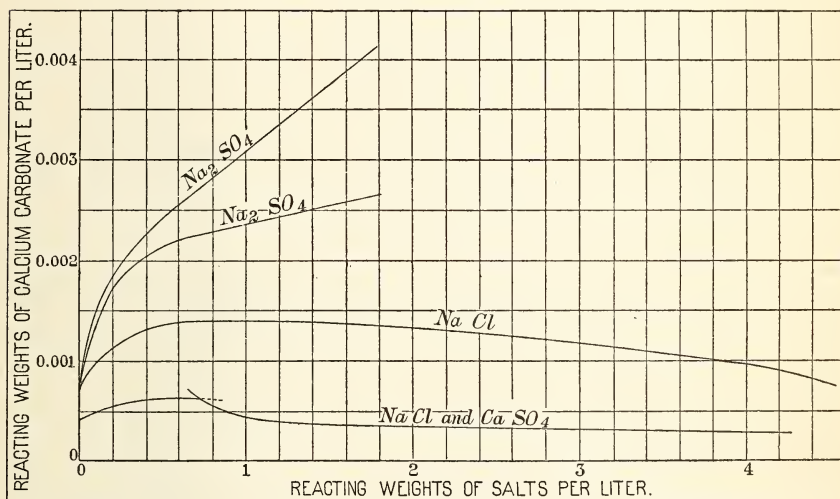


FIG. 10.—Diagram showing solubility curves for calcium bicarbonate in solutions of other salts. Results given in terms of reacting weights per liter.

In the accompanying figures (figs. 9 and 10) the calcium salt found to be soluble is plotted in all cases on the axis of ordinates and the amounts of other salt components of the solution on the axis of abscissas.

SOLUBILITY OF CALCIUM CARBONATE IN SODIUM CHLORIDE SOLUTIONS AT 25° C.

Air was passed through the solutions for twenty-seven days, the solutions being tested from time to time to determine when final equilibrium was reached, at which time they gave no reaction with phenolphthalein; that is to say, the solutions contained no normal carbonate dissolved in them.

At first sight this result appeared very surprising, but it is in line

with the observations of Treadwell and Reuter, and with the observations made in the laboratories of this Division in the study of the equilibrium between the normal carbonate and hydrogen carbonate of calcium, described in the preceding pages of this bulletin.

The results obtained in the analyses of the solutions are given in the accompanying table, which is self-explanatory.

TABLE XX.—*Calcium hydrogen carbonate soluble in aqueous solutions of sodium chloride at 25° C. and in equilibrium with air.*

Ca(HCO ₃) ₂ .		NaCl.	
Grams per liter.	R. wts. per liter.	Grams per liter.	R. wts. per liter.
0.1046	0.00065	0.000	0.000
.1770	.00110	9.720	.168
.2051	.00128	21.010	.362
.2152	.00134	30.301	.522
.2252	.00140	50.620	.872
.2212	.00138	69.370	1.195
.2172	.00135	98.400	1.695
.1971	.00123	147.400	2.540
.1569	.00095	234.500	4.040
.1227	.00076	262.300	4.520

These results are presented graphically in the accompanying figures.

The solubility curve presents a well-marked maximum point, corresponding to a solution containing in a liter about 56 grams, or 0.95 reacting weight of calcium hydrogen carbonate; that is to say, at the maximum point the corresponding solution would contain about 0.0561 gram of calcium—equivalent to 0.1402 gram of the normal carbonate. Hence it appears that the solubility of calcium carbonate under these conditions is about 80 times what it would be in pure water free from carbon dioxide.

In the series under consideration it was found that in the solution containing no sodium chloride there was 0.1046 gram per liter of calcium hydrogen carbonate, equivalent to 0.0592 gram per liter of the normal carbonate. Therefore the solubility of the calcium carbonate corresponding to the maximum point of the curve is 2.36 times its solubility in water in equilibrium with the air but containing no sodium chloride.

In general features the curve resembles the solubility curves for gypsum in solutions of sodium chloride or magnesium chloride; and the views expressed (in the discussion of the curves for those cases) as to the solution, transportation in the soil, and the subsequent reprecipitation of the slightly soluble calcium salt with changing concentration of the more soluble salts hold here. Of course the further complication—that the carbon dioxide in the gas phase in contact with the solution probably changes at the same time as the concentrations change with respect to the salts—enters and may effect the precipitation of the lime salt. But it should be remembered in this connection that calcium hydrogen carbonate is quite a stable compound in solu-

tion at ordinary temperatures, and does not yield up a part of its combined carbon dioxide as readily as do other hydrogen carbonates when the partial pressure of the carbon dioxide in the gas phase is lowered. It therefore seems probable that the concentrations of the solution with respect to sodium chloride would be the controlling factor in such a case as is under discussion.

SOLUBILITY OF CALCIUM CARBONATE IN SODIUM SULPHATE SOLUTIONS AT 24° C.

In this series of experiments normal carbonates were found to be present in the solutions of higher concentrations, even though successive examinations at intervals of weeks showed conclusively that the solutions had reached a final state of equilibrium and remained unchanged, even with the prolonged passage of air through them.

In the accompanying table the total amount of calcium in the solutions is given in terms of the equivalent in calcium hydrogen carbonate, although a part of the calcium should more properly be given as the normal carbonate. The actual amounts of the bicarbonate or hydrogen carbonate found in the solution are also given, and in the figure curves are plotted from both series of data. For purposes of comparison this is considered more desirable than giving the amounts of normal carbonate found, which could not well be illustrated in the figures.

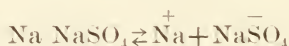
TABLE XXI.—*Solubility of calcium carbonate in aqueous solutions of sodium sulphate at 24° C., and in equilibrium with air.*

Total calcium calculated as $\text{Ca}(\text{HCO}_3)_2$.		Calcium actually dissolved as $\text{Ca}(\text{HCO}_3)_2$.		Sodium sulphate.	
Grams per liter.	R. wts. per liter.	Grams per liter.	R. wts. per liter.	Grams per liter.	R. wts. per liter.
0.6925	0.00057	0.0925	0.00057	0.000	0.0000
.1488	.00092	.1488	.00092	2.800	.0191
.1729	.00107	.1729+	.00107+	5.235	.0356
.2330	.00145	.2210	.00137	11.730	.0831
.3240	.00201	.3020	.00188	36.860	.2612
.3960	.00246	.3440	.00214	74.010	.5245
.4580	.00285	.3660	.00228	116.100	.8228
.5630	.00350	.3940	.00245	184.200	1.3054
.5910	.00367	.4060	.00252	213.700	1.5146
.6650	.00413	.4300	.00267	255.900	1.8135

It will be observed that the curves do not show maximum points, but that the solubility of the calcium carbonate, both in the form of normal carbonate and of hydrogen carbonate, steadily increases with increasing concentration of sodium sulphate. It is especially worthy of note that the solubility of the calcium carbonate is very much greater in solutions of sodium sulphate than in solutions of sodium chloride, although in the former case the slightly soluble compound calcium sulphate is presumably formed, and in the latter the very soluble substance, calcium chloride. Even granting that practically all the calcium sulphate formed again unites with the sodium sulphate

to form the soluble double sulphate, and making the further rather improbable assumption that this double sulphate dissociates in such a way as not to yield a calcium ion, the case does not become clear; for, at least in the higher dilutions, it would still be expected that the sodium chloride would have a greater solvent effect than the sodium sulphate. It is true that in the calculation of the data presented in this paper the reacting weight of sodium sulphate is based on the formula Na_2SO_4 instead of on the formula $1/2 \text{Na}_2\text{SO}_4$. An inspection of fig. 10 will show that even on this latter assumption the sodium-sulphate curve would lie well above the sodium-chloride curve. Assuming, therefore, that the effect of the sodium ions would be the same in the two cases, it appears that the SO_4 -ion has a greater effect than the Cl -ion in rendering the calcium carbonate more soluble.

Above a certain concentration (about 50 to 60 grams per liter) with respect to sodium sulphate the curves are practically straight lines; that is to say, the solubility of calcium carbonate in solutions above this concentration is directly proportional to the amount of sodium sulphate present. Assuming the mass law to hold, this indicates that at these higher concentrations the sodium sulphate dissociates as a binary electrolyte according to the scheme



From this point of view it would seem that the relative effects of the NaSO_4 -ions and the Cl -ions on the solubility of the calcium carbonate are to be compared, and that the first-mentioned ion is the more effective.

If it be assumed now that Ca -ion does not unite with the NaSO_4 -ion to form a more complex ion, but does unite with the Cl -ion to form complex ions, the greater solvent effect of the sodium sulphate over that of the sodium chloride becomes intelligible. It is to be frankly admitted, however, that this train of reasoning involves a number of assumptions, and that, while some evidences from other sources may be adduced in support, it can be advanced only tentatively. It further accents the very unsatisfactory state of our knowledge of solutions, especially in other than states of high dilution.

SOLUBILITY OF CALCIUM CARBONATE IN SODIUM CHLORIDE SOLUTIONS AT 25°C . IN CONTACT WITH CALCIUM SULPHATE IN THE SOLID PHASE.

The solutions were found to contain no normal carbonates. The effect of the dissolved calcium hydrogen carbonate on the solubility of the calcium sulphate has been discussed in the preceding paper. By referring to the figures it will be seen that the effect of the dissolved calcium sulphate on the solubility of the carbonate was of the

same general nature, but much greater in degree. With increasing concentration of sodium chloride the solubility of calcium carbonate gradually increases up to a maximum point, then drops suddenly, and finally decreases very gradually. The maximum solubility occurs in a solution containing about 40 grams per liter of sodium chloride. It will be remembered that the maximum solubility of the calcium sulphate, when calcium carbonate in the solid phase was also present, was in a solution containing from 80 to 85 grams per liter of sodium chloride.

While the effect of the presence of calcium carbonate on the solubility of calcium sulphate was shown to be slight in solutions containing less than 80 grams per liter of sodium chloride, it will be seen that the effect of the calcium sulphate on the solubility of the calcium carbonate is relatively great in all concentrations with respect to sodium chloride. Furthermore, the normal carbonate is entirely converted into hydrogen carbonate in the solutions. These facts are of great importance in considering the result of the application of calcium sulphate to soils containing calcium carbonate and sodium chloride and the much dreaded "black alkali" or sodium carbonate. Not only will the application of gypsum or land plaster to such soils reduce very much the amount of hydrogen carbonate in the soil solution and entirely eliminate the normal carbonate, but it greatly increases the amount of calcium soluble in the soil solutions. This fact alone would greatly increase the power of plants to resist the deleterious effects (other than an actual corrosion of the tissue) of an excessive amount of other soluble salts, as has been amply demonstrated by the results of some of the experiments made in the laboratory of this Division.

SUMMARY.

The results of this investigation show that sodium chloride in solution has an important rôle in causing the solution, transportation through the soil, and reprecipitation of calcium carbonate, and that this rôle is modified, but does not disappear, when calcium sulphate is present. The rationale of the application of gypsum or land plaster to soils containing "black alkali," or sodium carbonate, resulting from the action of sodium chloride upon calcium carbonate, is made apparent.

Sodium sulphate has been shown to have an astonishingly great effect on the solubility of calcium carbonate, the resulting solutions containing not only hydrogen carbonate, but normal carbonate as well. Further, there is no necessary precipitation of the lime carbonate with increasing concentration with respect to sodium sulphate; but the solubility of the lime carbonate steadily increases, with increasing amounts of sodium sulphate in the solution, up to the saturation point of this latter salt.

It is greatly to be regretted that time has not permitted an examination of the action of sodium sulphate on lime carbonate and sulphate simultaneously. The experience of the field parties of this Division that have worked on the alkali soils of the arid regions indicates that normal carbonates would not be present in the solution; but both the field work and an inspection of the analyses of the water-soluble constituents of soils containing these components indicate that hydrogen carbonate might be found to some considerable extent. It has, moreover, become important from the point of view of the effect of the soluble salts in the soil on plant culture to obtain an idea of the extent to which calcium in some form or other would be dissolved. The importance of the investigation for geological and drainage studies is evident. It is proposed to study this system at an early date.

CHEMICAL EXAMINATION OF ALKALI SOILS.

By ATHERTON SEIDELL.

INTRODUCTION.

In the course of the examination of several hundred alkali-soil samples in the laboratory of this Division, many difficulties have arisen in devising satisfactory methods for the systematic and rapid analysis of the portion of these soils readily soluble in water.

Some of the difficulties encountered have been mechanical, as the removal of suspended clay, which sometimes proves to be the source of a great deal of annoyance to the analyst. This disagreeable feature generally occurs when the total amount of soluble salts is very small, or when the alkali is small in amount and largely composed of soluble carbonates. The presence of the large quantities of dissolved organic matter sometimes found in the soil extracts, especially when much soluble carbonate is present, has given rise to a great deal of trouble, and has been given serious attention in the course of the analytical work of this laboratory. The equilibrium between normal carbonates and bicarbonates in aqueous solution has been found to have much importance in alkali studies, and the analytical problems attending it have been met in a satisfactory way.

Besides the examples cited many other points have been investigated and a large amount of information gathered in this laboratory along such lines. It is hoped that the results of the observations made and experience gained in this work may be of service to others who may have occasion to investigate chemically the alkali of arid soils.

The object of an "alkali analysis" is, first, to establish the chemical nature and relative composition of the constituents which form the readily water-soluble part of the soil; and, second, to obtain an approximate idea as to the amount of the readily soluble salts in the soil. The analytical operations, therefore, are confined to the investigation of the mineral substances contained in an aqueous extract of the soil. The amount of this soluble mineral matter may vary from almost nothing to 95 per cent or more of the soil sample.

It is evidently desirable that a criterion be established which would serve to distinguish the very soluble part of the soil as distinctly

"alkali" from the less readily soluble portion which, for that very reason, can not be considered as alkali in the sense of being material harmful to plant growth. Although no such distinction can be sharply made between the very soluble constituents and those which are relatively insoluble, but which become soluble with increased amounts of water and extended length of time for solution, there is sound reason for believing that the part of the soil which is "alkali" may be determined within narrow limits for practically all alkali soils. The analytical methods involved will be described in the course of this paper.

PREPARATION OF THE SOLUTION.

It may be considered that the alkali of a soil is composed of relatively soluble salts; therefore, for its solution is required only a relatively small amount of water and brief space of time. Suppose that a given alkali-soil sample contains half of its weight of soluble salts; taking 50 grams of the sample for analysis, probably a few hundred cubic centimeters of water would be sufficient to dissolve the 25 grams of alkali present within the space of a few hours. If we carefully separate the undissolved soil from the solution and then add another portion of water and allow it to digest an equal length of time, the amount of material which is dissolved by this second operation is ordinarily a very small fraction of the amount which the first portion of water extracted from the soil.

It is obvious that when a soil contains a very small quantity of readily soluble salts a rather smaller amount of water will be sufficient to effect the solution of these salts than when the amount of alkali is considerable. However, by using a somewhat larger amount of water than is necessary to dissolve the salts present no material error is introduced, since each aliquot portion of this solution contains practically the same amount of alkali as an aliquot portion of the solution made with an amount of water which, though smaller, is still enough to dissolve all the alkali salts in the given soil sample.

In regard to the less soluble constituents, as, for instance, calcium sulphate, it is certain that the use of a larger amount of water will surely mean a larger relative proportion dissolved from the soil. This is practically true only beyond rather wide limits in the amount of water used.

If a soil solution made with a relatively small amount of water is considered, the concentration of the more soluble ingredients, such as chlorides, sulphates, and carbonates of sodium and potassium, may be quite large. Considering the effect of increasing concentration of these electrolytes upon the more insoluble ones, as illustrated by the increased solubility of gypsum in sodium-chloride solutions described elsewhere in this bulletin, it is evident that the amount of these relatively insoluble constituents of alkali in solution may be very greatly increased under such conditions of increased concentration of the

more soluble electrolytes. Thus it may happen that the decrease, following the use of smaller amounts of water in making the soil solution, may in some degree compensate for the increase in the amounts of the more insoluble constituents dissolved with larger amounts of water.

In view of these considerations and for the sake of convenience and uniformity in the investigations upon all alkali-soil samples, it is the practice in this laboratory to place 50 grams of the soil sample for analysis in a large beaker and add to this one liter of distilled water. The solution is stirred vigorously several times and allowed to stand twenty-four hours. At the end of this time an amount of the supernatant liquid sufficient for the analysis is decanted through a filter paper into a flask.

The amount of water used in making the solution may appear to be somewhat liberal. Nevertheless it is evident that an error introduced in this manner would be of less importance than that which would result from using an insufficient amount of water, a consideration which should justify the procedure indicated. It seems altogether probable that the time limit of twenty-four hours allowed for the solution to come to final equilibrium with the material in the solid phase is rather too short, but it is not advisable to allow a longer time, since in many cases it is found that organisms collect in the solutions, and the indications are that the relative amounts of some of the constituents in the solution are markedly altered. In fact, it has been noticed that the growth of some of these organisms may be accompanied by the accumulation of soluble phosphates and, more frequently, nitrates.

The soil solution, made as above described, is quite clear whenever the amount of alkali in the soil is sufficient to flocculate the clay and smaller particles and so cause them to subside. This condition commonly occurs, but not always; for if the amount of alkali in the soil is very small, or small and largely composed of sodium carbonate, the clay will remain in suspension, and even when it is possible to separate it by filtration a very great amount of labor and time is required for its removal. The increased accuracy in the analytical results attained by filtering the muddy solution itself, instead of following the process described later, would hardly seem to justify the labor and time required for the filtration.

Quite recently Mr. Lyman J. Briggs, of this Division, has devised an apparatus by which clay can be successfully filtered from aqueous solutions at a rapid rate. It is expected that by the aid of this device even more satisfactory results will be attained than heretofore in the analysis of those alkali-soil samples which have so far presented the greatest difficulties.

Another difficulty will be experienced with the soil solution whenever the soil sample contains black alkali together with organic matter. In that event the solution may be quite free from suspended

clay, etc., but on account of the dissolved organic matter it is frequently very dark, and in such a condition makes the volumetric determination of carbonates, bicarbonates, and chlorides exceedingly difficult. This subject will receive further attention in the detailed descriptions of the analytical processes.

ELECTRICAL RESISTANCE OF THE SOLUTION.

Before commencing the analysis of the soil solution, made as explained above, it is customary to take the electrical resistance of the solution by means of the ordinary Wheatstone bridge, or the modification of the same devised for the use of the field parties of this Division.

Since by this method the number of ions in solution is at once approximately determined, some idea is obtained of the concentration of the solution prepared for the analysis; it is therefore possible to select an aliquot portion which will contain an amount of the ingredient looked for, most suitable for manipulation in any given analytical process.

If the electrical resistance of the solution in the cell used is very high (about 1,000 ohms or more at room temperature) it is known that the solution contains a very small amount of soluble salts, and it will be necessary to use quite large aliquot amounts of the solution in order to obtain enough of the various constituents for accurate determinations. A resistance as high as 1,000 ohms indicates an amount of total solids approximately 0.02 gram per 100 cubic centimeters of solution. This information, as regards the amount of salts which corresponds to a given electrical resistance in a soil solution, is of course only approximate, but still as found by experience is accurate enough to be very useful indeed to the analyst. For example, it is found that when the electrical resistance of the soil solution is something less than 1,000 ohms but more than 500 a portion of the solution consisting of 200 cubic centimeters or more must be used for the determination of each of the possible ions; when the resistance is near 200 ohms a 100 cubic centimeter portion of the solution will suffice. Frequently it happens that the alkali sample examined will contain as much as half its weight of soluble material. In such a case the electrical resistance of the solution being very low (10 or 15 ohms) will indicate that the amount of salts in solution is very great and it will become necessary to dilute the portions intended for each determination. That the solution has been diluted sufficiently will be indicated by a resistance that indicates an amount of salts which can be most accurately determined in 100 cubic centimeters portions of the solution.

A word of caution, based upon experience in this laboratory, may be of service in this connection. It has been found that it is not advisable to dilute the portion of the original soil solution intended

for carbonate and bicarbonate titrations, even when precaution is taken to boil the distilled water used for the dilution and thus free it from the carbonic acid which would cause the equilibrium between the carbonates and bicarbonates to be displaced in the direction of the bicarbonates. The results of the work of Dr. Cameron and Mr. Briggs, found elsewhere in this bulletin, verify this observation.

TOTAL SOLIDS DETERMINATION.

Total solids determinations, as made by evaporating to dryness in a platinum dish a given portion of the solution and weighing the desiccated material, are not only exceedingly unreliable, but are quite unnecessary for the analysis of soil solutions as practiced in this laboratory.

When such salts as are contained in alkali soil solutions are evaporated to dryness there will remain behind certain quantities of water of crystallization and also occluded water. The removal of this water is quite necessary for accurate determinations, but in many cases can be attained only by elevating the temperature of drying to dull redness. Also soil solutions frequently contain organic matter which requires a temperature of dull redness for its removal by combustion. Under the most favorable conditions, then, a temperature is required at which the volatilization of several of the constituents of the alkali will be possible. The results of total solids determinations may accordingly be very much too high or very much too low, depending in a great measure upon the temperature to which the material has been subjected.

Although confidence can seldom be placed in total solids determinations, they are sometimes serviceable in the estimation by difference of the amount of sodium when it has not been determined directly; also they may show a wide difference in results which would indicate that some of the possible ion determinations had been omitted. The sodium determinations are made directly, and the calculation as electrolytes of the ions determined insures the omission of none of the determinations. Therefore the total solids determination serves no important purpose in the analysis of alkali-soil samples as conducted in this laboratory, and is seldom made.

CARBONATE, BICARBONATE, AND CHLORINE DETERMINATIONS.

As indicated above, the equilibrium between the carbonates and bicarbonates in the soil solution is very readily displaced, and to a large degree. For this reason it is advisable to make these determinations as soon after the preparation of the soil solution as possible.

The method in use in the laboratory of this Division for the determination of the carbonates and bicarbonates in the solution is a volumetric one devised by Dr. Frank K. Cameron for the use of the field

parties. It is eminently adapted for accurate work, and is in all essentials a valuable laboratory method. The reactions involved and the practical applications of them are described in more detail by Dr. Cameron elsewhere in this bulletin.

The standard solution of acid potassium sulphate used contains 6.7584 grams of HKSO_4 per liter of solution, and is one-twentieth normal when considered in regard to replaceable hydrogen. To make the standard solution it is found advisable to dissolve, with heating, the weighed quantity of pure hydrogen potassium sulphate (HKSO_4) in a small amount of water and then make up the required number of liters. The solution may be standardized by titration against a standard ammonia or potash solution; it is not advisable, however, to precipitate the sulphion as barium sulphate and calculate the amount of the acid present from this determination. One cubic centimeter of the standardized HKSO_4 solution is equivalent to 0.002979 gram of carbonic acid ion (CO_3) or 0.003028 gram of hydrogen carbonic acid ion (HCO_3).

It seems most convenient in working with soil solutions, as previously described, to make the various determinations with 100 cubic centimeters aliquot portions; that is, to determine the grams of ions per each 5 grams of the soil. Therefore, unless it should otherwise be deemed inadvisable, as indicated by the electrical resistance of the solution, 100 cubic centimeters are placed in a beaker and titrated with the standard HKSO_4 solution for carbonates and bicarbonates and with standard $\text{N}/10 \text{ AgNO}_3$ solution for chlorides.

To the measured portion of the soil solution is first added several drops of a solution of phenolphthalein; in the presence of carbonates a characteristic bright red color will result; in the absence of the red color the solution may be titrated for bicarbonates, as described later. In case the presence of carbonates is indicated by the red color the solution is immediately titrated with the standard HKSO_4 solution, just to loss of color, and the reading on the burette taken. This reading multiplied by the factor for one cubic centimeter of the solution (0.002979) gives the grams of normal carbonic acid ions (CO_3) present in the soil solution. By this reaction the normal carbonates are converted to bicarbonates by reacting with hydrogen potassium sulphate (HKSO_4).

In clear solutions the change can be accurately noted. In the cases where the solution is blackened by organic matter or clouded with suspended clay, etc., it sometimes becomes exceedingly difficult to obtain satisfactory readings. But it has been found that by providing a titration stand having a glass top and a white surface a few inches below, to reflect the light up through the solution, the correct observation of the color change is greatly facilitated. In such cases the average of several closely agreeing titrations will usually furnish a sufficiently accurate determination for all practical purposes.

When the titration for normal carbonates has been completed there is added to the solution one drop of a solution of methyl orange indicator, and, without refilling the burette, the titration is continued until the delicate change in the color of the solution, due to the liberation of free, undissociated methyl orange, is observed. The reaction involved is the conversion of the bicarbonates to the double sulphates of potassium and the other bases present with the liberation of H_2CO_3 . Since methyl orange is not affected by the liberated H_2CO_3 in the solution, no change is observed until a very slight excess of HKSO_4 enters the solution. The complete conversion of all the bicarbonates present to sulphates is thus assured, and the amount of HKSO_4 necessary is an accurate measure of the amount of bicarbonates present.

The reading on the burette is taken at this change, and from this total reading is subtracted twice the first reading, and the resulting number of cubic centimeters is multiplied by the factor (0.003028) for HCO_3^- ions.

The change in the color of the methyl orange at the end of the reaction is very slight, being usually only a shade of yellow slightly more pink than previous to the change—the color being a mixed one, resulting from the unchanged indicator in excess as well as from the changed indicator. The sharpness of the change is quite pronounced, and can be best seen when very small amounts of the indicator are used. Although great care is required for its detection, the completion of the reaction as indicated thus is accurately established.

Experience has amply demonstrated the advisability of using but small amounts of the methyl orange in the solution. The titration should be regarded as completed at the first change of color which can be detected in the indicator.

As might be supposed, anything but a clear solution being taken for this titration very greatly hinders the success of the determination; in some cases great accuracy is precluded. An indicator more suitable than methyl orange, for use with solutions which are colored, has been sought for, but with results not altogether satisfactory, although Congo red may be used to advantage under certain conditions, as pointed out by Dr. Cameron.¹ The problem requires the use of an indicator with the most marked differences in color in solutions which are alkaline and those which are acid. In addition, the strength of the indicator should be greater than carbonic acid, in order that the liberated H_2CO_3 should not itself affect the condition of the indicator during the reaction.

Another point worthy of attention, in regard to this volumetric method for the determination of carbonates and bicarbonates in aqueous solutions, is suggested by the experience gained in this laboratory. In addition to small particles of insoluble carbonates of

¹ See paper on The Estimation of Alkali Carbonates and Bicarbonates, p. 77.

alkaline earths, which are found in these muddy solutions, the clay itself may contain certain quantities of insoluble carbonates. When such soil solutions are titrated with the acid potassium sulphate, a part of the hydrogen potassium sulphate (HKSO_4) in the standard solution is used up in the reaction with these insoluble carbonates, and the apparent results for soluble carbonates will be somewhat too high. Errors due to this cause must be carefully guarded against, and require the greatest care for their avoidance.

It should be clearly understood in this connection that the ratio of normal carbonates to hydrogen carbonates, as determined in the laboratory, may lead to erroneous conclusions regarding the conditions in the field. It is certain that in transit from the field to the laboratory, with the drying out and other changes in the soil, the ratio of the normal carbonate to hydrogen carbonate must be materially changed. It is therefore advisable, when this ratio under field conditions is desired, that the determination should be made at the time the sample is taken. It is desirable that this ratio as determined in the field should accompany the statement of the analysis made in the laboratory. This has not always proved practicable in the past, but with a realization of the importance of the matter, it is intended that the field ratio shall be given in connection with the statement of analyses in future reports.

Upon the completion of the titration for the carbonates and bicarbonates the chlorides may be determined in the same solution by titration with standard silver nitrate. To the solution is added one drop of a saturated solution of potassium chromate (K_2CrO_4) and the standard one-tenth normal AgNO_3 solution slowly run in from the burette until the appearance of the red color, due to the formation of silver chromate, is recognized. This reaction is usually very sharp and the end may be most accurately determined. The number of cubic centimeters read off is multiplied by the factor (0.003518), and the result is the grams of chlor ions in the solution titrated.

OTHER DETERMINATIONS.

The only other acid ion found in alkali soil solutions to any large extent is sulphion (SO_3). The estimation of this in clear solutions is made by the usual method of precipitation and weighing as BaSO_3 . In dealing with soil solutions which contain organic matter or suspended clay, etc., a very slight excess of hydrochloric acid is added and the solution boiled. In practically all cases the organic matter or clay will flocculate and can be filtered from the solution. There seems to be no appreciable error introduced by the solution of the insoluble sulphates from the suspended matter with the very small amount of hydrochloric acid which is required to bring about flocculation.

This method of clearing solutions of suspended matter is not per-

missible, when the solutions are intended for the basic ion determinations, on account of the relatively large amounts of the bases which may be dissolved from the suspended matter by the hydrochloric acid. For this reason the filtrate from the sulphion (SO_4) determination is to be used for the sodium (Na) and potassium (K) ion determinations only when the original soil solutions is clear of suspended matter.

In addition to the four acid ion determinations described above, a qualitative examination is always made for nitrates and phosphates. When it appears that an amount of these constituents is present sufficient for quantitative determination, the nitrates are determined by the Ulsch method and the phosphates by the molybdate method.

The occurrence of borates in alkali soils which give promise of ever having any agricultural value is so rare that it very seldom happens that such a determination is made necessary in the work of this laboratory. Although the experience with this determination in the laboratory of this Division has been somewhat limited, the Gooch method has yielded the most satisfactory results.

The amount of silicic acid ions (SiO_3) which will be dissolved from an alkali soil by water is usually inappreciable; hence it is seldom found necessary to make the determination in the soil solution. Occasionally it is desirable to make this determination, especially in solutions made from soils containing much soluble carbonate. The determination is then carried out in the conventional way by adding an excess of hydrochloric acid to the solution and evaporating to dryness several successive times to precipitate the silica in an insoluble form suitable for separation by filtration. Some care must be taken that gypsum does not precipitate at the same time and interfere with the determination, but this latter difficulty is seldom encountered.

Whenever it is necessary to obtain the soil solution free from suspended material for some of these determinations, especially from the basic constituents, besides the device of Mr. Briggs referred to above, two methods of procedure have suggested themselves and have been tried in this laboratory.

The muddy solution was evaporated to dryness and the dish gently heated to cake the clay. The material was then taken up with water and filtered. Occasionally it was necessary to repeat the process in order to get rid of all the suspended material. A serious objection to the procedure arose whenever calcium salts and carbonates or sulphates were present to any extent; for in such cases a considerable portion of the calcium would be precipitated as the carbonate or sulphate, and, while they would undoubtedly go into solution again in the course of time, the rate of solution for these salts is so slow that there can hardly be any question that much of the calcium was not taken up but left in the clay residue. The same general considerations, but probably to a lesser degree, apply also to the magnesium.

A better method than this consists in flocculating the suspended matter in the solution with a very small amount of ammonia alum and then filtering off the clear solution. The experience in this laboratory has shown that both of these methods are open to objections. The experimental difficulties are less in using the latter method, and the errors are usually negligible; therefore this method is to be preferred.

The analytical methods for the base ion determinations in soil solutions, when they are free from suspended matters are those most commonly applied. Calcium is precipitated as the oxalate and, after blasting, weighed as the oxide; magnesium is determined as magnesium pyro-phosphate; sodium and potassium are separated together in the usual manner and weighed as the chlorides; the potassium is separated from the sodium as potassium platonic chloride.

The shortcomings of this last method are well known to all, and it is to be regretted that a more satisfactory analytical method for the determination of sodium and potassium has not been devised. In spite of the fact that the very accurate determination of sodium is almost impossible, it is apparent that sodium determinations made in this way are much to be preferred to those statements of results which indicate the amount of sodium present by "difference."

CALCULATION OF ANALYSES.

The analytical methods, as previously described, give the grams of each of the ions determined in 100 cubic centimeter portions of the soil solution, or the grams of ions per each 5 grams of the soil sample. These results are tabulated and the sum, after being divided by 5 and two decimal places pointed off to the right, gives the percentage of "alkali" in the soil sample.

Since the analysis has been made upon an aqueous solution of a number of salts, the acid ions determined must be exactly sufficient to combine with the base ions determined regardless of the manner in which the combinations are made. The analysis is regarded as satisfactory when this condition is fulfilled and duplicate determinations are deemed necessary only when there is an error in the analysis—indicated by a discrepancy in the calculation of the ion determinations as electrolytes.

The manner in which the ions are combined is arbitrary, and it must be strongly urged that great care be exercised in drawing conclusions in regard to an alkali soil from the consideration of an analysis expressed as salts, although much useful information can sometimes be obtained from this source.

No special justification is claimed for the method of calculating the analysis as practiced in this laboratory. It is evident that the ions as found in the soil solution really exist in all the combinations possible as well as in the dissociated state. It is merely a matter of conven-

ience that justifies the combination of the base ions in the following order: Ca, Mg, K, and Na with the acid ions in the following order: SO_4 , Cl, CO_3 , and CHO_3 . When these calculations are completed the total of the electrolytes thus stated must be equal to the total of the ions as actually determined.

Finally, from these results the percentage composition of the alkali, as expressed in ions and electrolytes, is calculated. The results are stated in this form, since it is the relative composition of the alkali which the analysis is mainly designed to make clear.

SUMMARY.

The method for the examination of alkali soils as described in this paper, presents the following features:

1. The aqueous solution of the soil alkali is made under similar conditions in all cases.
2. The electrical resistance of the soil solution is used in facilitating the analytical processes.
3. A direct determination of the total solids in the soil solution is not made.
4. A unique, satisfactory, and accurate volumetric method is used for the determination of carbonates and bicarbonates.
5. All the constituents, including sodium, are determined directly, and no results are obtained by difference.
6. The possible necessity for duplicate determinations is made evident by the calculation of the results obtained.
7. Finally, the report of the analysis includes the percentage of alkali present in the soil and the relative percentage composition of this alkali; it is stated in terms of the possible ions present in the solution as well as their combinations as electrolytes.

For the convenience of those who may wish to apply the methods for alkali soil examination here described, there is appended at the end of this paper a table of the factors, with the logarithms of the same, found necessary for the calculation of the analytical results.

ESTIMATION OF CARBONATES AND BICARBONATES IN AQUEOUS SOLUTION.

By FRANK K. CAMERON.

NATURE OF THE PROBLEM.

The estimation of carbonates and bicarbonates in aqueous solution is a problem frequently presented in this laboratory. It has been found that the method first suggested by Winkler, of which Küster¹ has given a good description, is very well adapted for this purpose when modified as I have suggested.² The method depends upon the fact that carbonic acid ($=\text{CO}_3$) or hydrogen carbonic acid ($-\text{HCO}_3$) is a stronger acid than phenolphthalein but weaker than methyl orange. If phenolphthalein be added to a solution containing alkaline carbonates it will show the well-known alkaline reaction, on account of the hydrolized free base in the solution, and will continue to do so until all the free base which may be formed by the hydrolysis of the normal carbonate has been neutralized. The hydrogen carbonates or bicarbonates do not themselves show an alkaline reaction with phenolphthalein; but if methyl orange be added to the solution, being a stronger acid than the carbonic acid, it will show its characteristic reaction toward the base as though carbonic acid were not present, qualitatively at least.

DESCRIPTION OF THE METHOD.

The mechanism of the method consists in titrating with a standard solution of hydrogen potassium sulphate (6.7585 grams HKSO_4 per liter), using phenolphthalein as indicator until loss of color. The reading taken at this point gives the equivalent of normal carbonates present. Methyl orange is then added and the titration continued—without refilling the burette, but starting from the point where the last reading was taken—until the change of color, and the reading again taken. This final reading, *less twice* the first reading, gives the equivalent of the bicarbonates present. This procedure has become

¹Zeits. für anorg. Chem., **13**, 127 (1896).

²Report 64, U. S. Department of Agriculture; Am. Chem. Jour., **23**, 471 (1900).

especially important, since it has been shown from the work of others¹ and by extended investigations in this laboratory that solutions of carbonates almost invariably contain bicarbonates as well, especially when allowed to stand in contact with the air. Under such circumstances a definite equilibrium between the carbonates and bicarbonates is established, depending upon the concentration and temperature. Moreover, the distilled water in most laboratories, especially when first prepared, is rich in dissolved carbonic acid, so in making up solutions of alkaline carbonates, bicarbonates are at once formed.

Attention has been called by Mr. Briggs to the fact that considerable quantities of carbon dioxide are absorbed or condensed on solid surfaces, such as glass beads, soil grains, etc. When such surfaces are washed with an alkaline solution bicarbonates will be formed, and if not too concentrated with respect to the normal carbonate the solution may lose its alkaline character (toward phenolphthalein, for instance), a fact amply verified by experience. This process is probably an important one in nature, especially when quantities of sodium carbonate or black alkali occur in the soil. The composition of the solution formed under such conditions is readily determined by the method under discussion, and this is regularly done by the field parties of this division when working in alkali regions. Since the method has come into somewhat extended use in the hands of nonprofessional chemists, certain difficulties and misconceptions have developed which make it seem desirable to give more explicit explanations, and this opportunity is taken to do so.

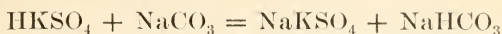
To obtain a specimen of the acid of the exact composition indicated by the formula HKSO_4 is probably a very difficult matter, and the effort to do so is not worth while, as has been pointed out in another place. A reasonably pure substance will answer very well and can readily be obtained from the dealers. For the accurate work in this laboratory the standard acid solution is always compared with another standard solution, generally by titrating both it and a carefully prepared tenth normal ($\text{N}/10$) HCl solution against a solution of potassium hydrate free from carbonates. In field work experience has shown that the solutions made from weighed portions of the chemically pure material obtained from a responsible dealer is sufficiently accurate for all purposes.

THEORETICAL BASIS OF THE METHOD.

For practical purposes hydrogen potassium sulphate may be regarded as a monobasic acid which will yield the ions H^+ and KSO_4^- , although it is well known that this is not strictly true. On this

¹ That this is true for the carbonates of magnesium has been suggested by Treadwell and Reuter (*Zeits. für anorg. Chem.*, **17**, 178 (1898)). That it is true for the sodium and potassium salts has been clearly demonstrated by the work of Mr. L. J. Briggs and the author.

assumption a solution containing 6.7585 grams of the acid per liter will be a twentieth normal (N/20) solution; that is, containing a 0.05 gram equivalent of hydrogen per liter, or 1 gram equivalent of hydrogen in 20 liters of solution. Since the reaction with sodium carbonate is expressed by the equation

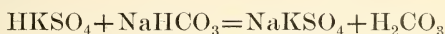


[Phenolphthalein as indicator].

it is evident that one reacting weight of H_2SO_4 is equivalent to one reacting weight of normal sodium carbonate. But sodium carbonate (Na_2CO_3) is a bibasic salt, and 1 cubic centimeter of the twentieth normal (N/20) acid will be equivalent to 1 cubic centimeter of a tenth normal (N/10) solution of the carbonate. To obtain the weights in grams of the several equivalents multiply the number of cubic centimeters of acid used by the following factors:

Normal sodium carbonate, Na_2CO_3	0.005261
Total sodium combined as normal carbonate002288
Sodium converted to form of bicarbonate during the titration001144
CO_3 ions combined as normal carbonate002978

With sodium bicarbonate the reaction is expressed by the equation:



[Methyl-orange as indicator].

Again we have one reacting weight of the acid equal to one reacting weight of the sodium hydrogen carbonate; but as we do not regard this latter substance (in this connection) as an acid but as a sodium salt of a monobasic acid $\text{H}(\text{HCO}_3)$, we have 1 cubic centimeter of the twentieth normal (N/20) acid equivalent to 1 cubic centimeter of the twentieth normal (N/20) salt solution. It is obvious that for each reacting weight of sodium carbonate originally in the solution there will be a reacting weight of sodium hydrogen carbonate after the titration with phenolphthalein as indicator. Therefore as many cubic centimeters of acid as were required for the titration with phenolphthalein must be added to neutralize this sodium hydrogen carbonate thus formed before the titration for this salt originally present may properly be begun. This will explain the directions given above for reading the burette. To obtain the weight in grams of the several equivalents, multiply the number of cubic centimeters of acid required by the factors:

Sodium hydrogen carbonate, NaHCO_3	0.004172
Sodium combined as hydrogen carbonate001144
HCO_3 -ions combined as hydrogen carbonate003028

With the potassium salts, both the carbonate and bicarbonate, the reactions are strictly analogous to those with the sodium salts, and precisely similar reasoning holds throughout. The statements in the

foregoing paragraphs need be changed only as to the absolute values of the factors, which may be tabulated as follows:

Titration of normal carbonate.

[Phenolphthalein as indicator.]

Normal potassium carbonate, K_2CO_3	0.006860
Total potassium combined as normal carbonate003882
Potassium converted to the form of bicarbonate during the titration.....	.001942
CO_3 -ions combined as normal carbonate002978

Titration of bicarbonate.

[Methyl orange as indicator.]

Potassium hydrogen carbonate, $KHCO_3$	0.004969
Potassium combined as hydrogen carbonate001942
HCO_3 -ions combined as hydrogen carbonate003028

MODIFICATIONS FOR ALKALINE EARTHS.

With solutions of magnesium carbonate and bicarbonate certain differences are introduced of which account must be taken. With magnesium carbonate the reaction appears to be expressed by the equation



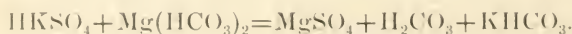
[Phenolphthalein as indicator.]

One reacting weight of the acid is equivalent to one reacting weight of the magnesium carbonate. Magnesium carbonate being a bibasic salt, 1 cubic centimeter of the twentieth normal (N/20) acid is equivalent to 1 cubic centimeter of a tenth normal (N/10) solution of magnesium carbonate. The amount in grams of the constituents determined can be obtained with the following factors:

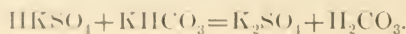
Normal magnesium carbonate, $MgCO_3$	0.004183
Magnesium combined as normal carbonate001205
CO_3 -ion combined as normal carbonate002978

As will be seen from the last equation given, an equal amount of the acid to that required for the titration with phenolphthalein as indicator must be added to neutralize the potassium hydrogen carbonate formed, before the titration for magnesium bicarbonate with methyl orange as indicator may proceed.

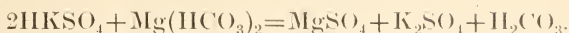
The reaction with magnesium bicarbonate apparently takes place in two stages:



But the potassium hydrogen carbonate resulting from the reaction, reacts as an alkali toward the stronger electrolyte, methyl orange, which is used as an indicator for this titration. A further addition of the acid must be made to neutralize this salt, according to the equation:



If the complete reaction as indicated by the two equations given be brought together in one expression we have:



From this last equation it appears that two reacting weights of the acid are required to balance one reacting weight of the *bibasic* magnesium bicarbonate. Therefore, 1 cubic centimeter of the twentieth normal (N/20) acid will be equivalent to 1 cubic centimeter of a twentieth normal (N/20) solution of the salt. To determine the weight of the salt equivalents determined, the following factors may be used:

Magnesium bicarbonate, $\text{Mg}(\text{HCO}_3)_2$	0.0036305
Magnesium combined as bicarbonate.....	.0006025
HCO_3 -ion combined as bicarbonate.....	.0030280

The reactions with solutions of calcium salts are strictly analogous to those with the magnesium salts. The factors may be tabulated as follows:

Titration of normal carbonate.

[Phenolphthalein as indicator.]

Normal calcium carbonate, CaCO_3	0.004966
Calcium combined as normal carbonate.....	.001988
CO_3 -ion combined as normal carbonate.....	.002978

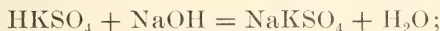
Titration of bicarbonate.

[Methyl orange as indicator.]

Calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$	0.004022
Calcium combined as bicarbonate.....	.000994
HCO_3 -ion combined as bicarbonate.....	.003028

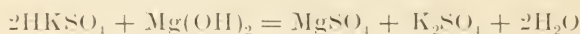
MODIFICATIONS IN PRESENCE OF A FREE BASE.

The method is readily applicable to a case where there is an excess of free bases. The titrations are made as before, but in this case the difference between the final reading and the first reading gives the equivalent of normal carbonates present; and the first reading, less this difference, gives the equivalent of free base present. Titrating with phenolphthalein as indicator, the free base—for instance, sodium hydroxide—is first neutralized according to the equation:

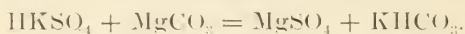


but the solution will still show an alkaline reaction from the sodium carbonate, which will not disappear until the carbonate has been converted into bicarbonate according to the equation already given. But if methyl orange be now added and the titration continued, just so much acid will be required to neutralize the bicarbonate as was required to convert the normal carbonate to bicarbonate. Since in

both titrations the reactions take place, reacting weight for reacting weight, 1 cubic centimeter of the twentieth normal (N/20) acid is equivalent to 1 cubic centimeter of a twentieth normal (N/20) salt solution. In the case of magnesium compounds the titration, with phenolphthalein as indicator, involves the reactions given in these equations:



and



If methyl orange be now added, and the titration continued, the reaction will be between the potassium hydrogen carbonate formed in the first titration and the standard acid. This reaction, we have already seen, takes place reacting weight for reacting weight. And, as will be seen from the equation, one reacting weight of the potassium hydrogen carbonate is equivalent to one reacting weight of the magnesium carbonate, and it may be assumed that 1 cubic centimeter of the twentieth normal (N/20) acid is equivalent to 1 cubic centimeter of the tenth normal (N/10) solution of the bibasic magnesium carbonate. But with respect to the magnesium hydrate, the equation shows that two reacting weights of the acid are equivalent to one reacting weight of the hydrate. Therefore 1 cubic centimeter of the twentieth normal (N/20) acid is equivalent to 1 cubic centimeter of a twentieth normal (N/20) solution of the bibasic magnesium hydrate. From a consideration of these facts the following factors were calculated:

Table of factors.

Sodium hydrate, NaOH.....	0.001988
Sodium combined as hydrate001144
Sodium carbonate, Na ₂ CO ₃005261
Sodium combined as carbonate002288
Potassium hydrate, KOH.....	.002785
Potassium combined as hydrate001941
Potassium carbonate, K ₂ CO ₃006860
Potassium combined as carbonate003882
Magnesium hydrate, Mg(OH) ₂0014465
Magnesium combined as hydrate0006025
Magnesium carbonate, MgCO ₃004183
Magnesium combined as carbonate001205
Calcium hydrate, Ca(OH) ₂001838
Calcium combined as hydrate000994
Calcium carbonate, CaCO ₃004966
Calcium combined as carbonate001988

EXTENSION OF THE METHOD TO INCLUDE ESTIMATION OF CHLORIDES.

One great advantage in using this method lies in the fact that chlorides, if present in the original solution, can be readily estimated

volumetrically in the same sample taken for the estimation of the carbonates or the free bases.¹ Normal carbonates, or the free bases, if present, would of course interfere with a titration for chlorides with standard silver-nitrate solution. But when the titration with the standard hydrogen potassium sulphate (HKSO_4) solution has been completed, these objectionable components have been converted either to neutral sulphates or to bicarbonates. Neither of these will interfere with the precipitation of chlorine by the silver salt. Silver sulphate, as is well known, is a readily soluble salt. It has been established that silver bicarbonate (if it exists at all²) is at least twenty-three times as soluble as the slightly soluble normal carbonate.³ But the important point in this connection is that it may be regarded as a fairly soluble salt, and, under the conditions likely to be met in analytical practice, does not interfere with the precipitation of chlorine by silver nitrate. It is only necessary, then, on the completion of the titration with the acid potassium sulphate solution, to add a single drop in excess to prevent any inversion⁴ of the bicarbonates, then add a drop or two of potassium chromate as an indicator, and proceed with the titration with the silver nitrate solution. The precaution of adding a drop or two in excess of the hydrogen potassium sulphate solution is often an important one. It can seldom or never cause any embarrassment by affecting the solubility of the silver chromate at the end of the titration, when used in the amount indicated. On the other hand, it is to be remembered that potassium chromate, consisting of a strong base-forming metal with a comparatively weak acid, is considerably hydrolyzed in water, giving an alkaline reaction. The desirability of preventing this, especially in such a case as we are considering, is obvious.

It may be worthy of remark here that our experience indicates the desirability of using very small quantities of the chromate as indicator—as little, in fact, as will give a distinct color to the solution, although this will vary somewhat with the eye of the individual analyst. At the end of the reaction between the chloride and the soluble silver salt, if any considerable amount of the chromate be present, the strong yellow color it imparts to the solution, together with that of the red silver chromate first formed, gives a disagreeable mixed color of an indefinite shade, and to accomplish a sharp titration is very difficult under such circumstances.

¹Am. Chem. Jour. 23, 481 (1900).

²Mendeleeff, in his Principles of Chemistry, implies that silver hydrogen carbonate can not exist.

³At 21° C. the solubility of silver hydrogen carbonate (AgHCO_3) is 0.942 gram per liter; silver carbonate (Ag_2CO_3), 0.0399 gram per liter.

⁴See Am. Chem. Jour. 23, 471 (1900).

OBJECTIONS TO THE METHOD.

Küster¹ has urged as an objection to Winkler's method that the end point of the titration, with methyl orange as indicator, is too uncertain. Here, again, the difficulty can at least be much diminished by using a minimum amount of the indicator. Experience in this laboratory indicates that the trouble in this case is also owing to a mixed color, arising from the color of the unchanged indicator blending with and more or less masking the color of the changed indicator. Several workers in this laboratory have had frequent occasion to use the method, and, after very little practice, determinations made quite independently show remarkably good agreement. A long and careful examination of this point has demonstrated that by using very small quantities of the methyl orange the most accurate results are obtained by titrating just to the first appearance of change of color. This experience has been very fully confirmed by that of other workers in this laboratory and is in direct opposition to the views of Küster, who advises titrating to some definite tint. As an example, some results are given in Table XXII, made with a solution of sodium carbonate prepared from chemically pure material (obtained from Eimer and Amend) and distilled water, which had previously been boiled for a long time to get rid of any excess of dissolved carbon dioxide. These results are not especially selected, but are given just as they were made, with the ordinary care and without rejecting any determinations.

The first column gives the number of cubic centimeters of the carbonate solution taken; the second, the number of cubic centimeters of the standard HKSO_4 solution required to titrate to loss of color with phenolphthalein as indicator; the third, the number of cubic centimeters of the standard acid required after adding the methyl orange and continuing the titration; the fourth, the difference of the two titrations, respectively, and the fifth, the amount required for 1 cubic centimeter, using methyl orange as the indicator.

TABLE XXII.—*Titration of Na_2CO_3 solution with N/20 HKSO_4 , using very small quantities of methyl orange as indicator.*

Quantity of Na_2CO_3 solution.	Quantity of N/20 HKSO_4 required.		Differences in the titrations.	N/20 HKSO_4 = 1 c.c. Na_2CO_3 solution, methyl orange as indicator.
	With phenolphthalein.	With methyl orange.		
C.	C. C.	C.	C. C.	C. C.
10	4.60	9.15	4.55	0.915
10	4.55	9.13	4.58	.913
10	4.60	9.12	4.52	.912
25		22.85		.914
				.9135

The results here presented must be regarded as quite satisfactory, and it would seem that used in the way just indicated satisfactory results can be obtained with methyl orange. Nevertheless, it must be admitted that the difficulty in its use is a real one, and is greater with some individuals than with others, as the color change is certainly a difficult one for many analysts to distinguish even under the most favorable conditions.

CONGO RED AS AN INDICATOR.

The desirability of finding a more suitable indicator became evident, all the more so in view of certain difficulties experienced by our field parties working in the alkali or arid regions of the West. This method now forms a part of their regular equipment for the examination of alkali soils in the field. But very frequently they are obliged to deal with the turbid solutions containing much suspended clay in which the color absolutely precludes the use of the methyl orange, unless large quantities be used and a decided excess of acid be run in to obtain a sufficiently definite color change. After various attempts to find an acid indicator stronger than carbonic acid that would give well-marked color changes, it was at last found that "Congo red" fulfilled the requirements quite satisfactorily. On the basis of some preliminary experiments it has been adopted by the field parties, with generally satisfactory results. An examination of the conditions best adapted to its use was deemed advisable, however, and the results are here presented.

Congo red is now on the market in considerable quantities. It can be obtained readily in very satisfactory condition, and is now widely used as an indicator, to a great extent taking the place of litmus. The color change is very similar to that of litmus, but more marked, and in the reverse order, being a strong red in alkaline solutions and a heavy blue or blue-black in acid solutions. For the purpose of the experiments here described a solution of sodium carbonate (Eimer and Amend, c. p.) of unknown strength was prepared, using distilled water which had been boiled for a long time to expel carbon dioxide. The results are presented in tables XXIII, XXIV, XXV, and XXVI. Those given in Table XXIII were obtained by an assistant in the laboratory, who had had no previous experience with the method; titrations Nos. 1 and 2, made in beakers, being intended merely as rough determinations to familiarize him with the method. The other titrations were made in porcelain dishes. No titrations whatever have been discarded, all being presented as they were obtained and without preference. The methyl orange for all the titrations in which its use is described in this paper was prepared by dissolving 1 gram in 200 cubic centimeters of water. A single drop only was used for a

titration. Even smaller quantities would have been preferable. The Congo red was prepared by making a saturated solution in 30 per cent alcohol. The first column of the table gives the number of the experiment; the second column, the number of cubic centimeters of the sodium carbonate solution; the other columns, the number of cubic centimeters of the hydrogen potassium sulphate solution required, the indicator used being stated at the head of the column:

TABLE XXIII.—*Titrations of Na_2CO_3 solution with $N/20$ H_2SO_4 for the purpose of comparing methyl orange and Congo red as indicators.*

No.	Quantity of Na_2CO_3 solution.	Quantity of $N/20$ H_2SO_4 required—		
		With phenolphthalein	With methyl orange.	With Congo red.
	c. c.	c. c.	c. c.	c. c.
1	25	21	42	-----
2	25	-----	42.1	-----
3	25	20.4	42.1	-----
4	25	20.9	42.05	-----
5	25	20.65	42.05	-----
6	25	20.5	-----	42.3
7	25	20.8	-----	42.3

A series of titrations was then made to determine at what point the titration should cease after the color change began. It was clearly demonstrated that the best procedure was to titrate until no further change of color could be observed—in striking contrast to what was found advisable when methyl orange was used. This point established, the titrations presented in Table XXIV were made, the statement in brackets at the right referring to the amounts of indicator used. The titrations were made in porcelain dishes:

TABLE XXIV.—*Titrations of Na_2CO_3 solution with $N/20$ H_2SO_4 , using varying amounts of Congo red as indicator.*

No.	Quantity of Na_2CO_3 solution.	Quantity of $N/20$ H_2SO_4 required—		
		With phenolphthalein.	With methyl orange.	With Congo red.
	c. c.	c. c.	c. c.	c. c.
8	25	20.6	42.10	-----
9	25	20.6	-----	42.05 [2 drops]
10	25	-----	-----	42.05 [1 drop]
11	25	-----	-----	42.15 [4 drops]
12	25	-----	-----	41.7 [1 c. c.]
13	25	-----	-----	41.6 [1 c. c.]

The low results obtained in experiments 12 and 13 were obviously due to inability to follow the color change in the presence of such densely colored solutions as were obtained with such amounts of indicator in a porcelain dish. Two titrations were then made in glass

beakers so arranged that light passed through the solutions from the bottom. The results are given in Table XXV:

TABLE XXV.—*Titrations of Na_2CO_3 solution with $\text{N}/20$ H_2SO_4 , using large quantities of Congo red as indicator.*

No.	Quantity of Na_2CO_3 solution.	Quantity of $\text{N}/20$ H_2SO_4 required.
	c. c.	c. c.
14	25	42.10 [1 c. c.]
15	25	42.05 [1 c. c.]

It would appear from the results given in Tables XXIV and XXV that very satisfactory titrations can be made with Congo red as indicator, and that considerable quantities of the indicator may be used if care be taken to pass a strong beam of light through the solution. This point is one of great importance where the method is used in the field—for instance, in solutions which hold a considerable quantity of matter in suspension, often strongly colored. The temptation to use a large quantity of indicator is often great under such circumstances, and the tendency to obtain too low readings on account of the inability to clearly distinguish the end point of the reaction in the dark-colored opaque fluid resulting, is equally great. This fact has been amply verified by general experience with the method. Further tests were made in the laboratory by suspending clay in some sodium carbonate solutions and titrating with various amounts of the indicator present. While fairly concordant results were obtained, there was an undoubted tendency toward low readings when much of the indicator was present.

Solutions were now prepared, each containing 10 cubic centimeters of the sodium carbonate solution already described and 5 cubic centimeters of a $\text{N}/5$ sodium chloride solution. These were titrated in the usual way. After completing the titration with the hydrogen potassium sulphate solution a drop or two of a saturated solution of potassium chromate was added. The strong yellow color appeared at once, with no evidence of any interference from the Congo red present. The results of the titrations are given in Table XXVI, in which the second column represents the amount of Congo red taken as indicator. The third column gives the number of cubic centimeters of the hydrogen potassium sulphate solution required, and the fourth column the number of cubic centimeters of $\text{N}/10$ silver nitrate solution required:

TABLE XXVI.—*Titrations for carbonates and chlorides, when Congo red is used as an indicator.*

No.	Amount of Congo red.	Quantity of $\text{N}/20$ H_2SO_4 required.	Quantity of $\text{N}/10$ AgNO_3 required.
		c. c.	c. c.
16	2 drops	16.8	9.95
17	1 drop	16.8	10
18	2 drops	16.8	10

With the amount of indicator used no difficulty whatever was experienced in getting sharp readings and very satisfactory determinations for the chloride present. Using large amounts of Congo red, however, more or less difficulty was experienced in determining the chlorides sharply. Apparently silver forms a compound with Congo red which gives a solution with a color very nearly that of silver chromate, so that the end reaction in the titration is more or less masked thereby. Under no circumstances, when chlorides are to be determined, is Congo red as satisfactory as methyl orange, and this latter is to be preferred when the conditions of the work in hand will admit of its use.

With potassium salts the method is quite as satisfactory as with sodium salts, and it does not seem worth while to present any figures in further demonstration of it.

A solution of magnesium carbonate in water saturated with carbon dioxide was examined. Three 10 cubic centimeter portions were titrated with the hydrogen potassium sulphate solution, using Congo red as indicator, with the following result, the figures in brackets indicating the quantity of indicator used:

19.6 [1 drop] 19.7 [2 drops] 19.6 [1 drop]

Using larger amounts of the indicator, similar results to those with the sodium carbonate were obtained—a tendency to obtain too low readings when much indicator was used. In this case also chlorides could be estimated quite readily if too much Congo red had not been used. These statements hold as well for solutions containing calcium carbonate or bicarbonate.

DIFFICULTIES IN THE PRESENCE OF CARBONATES IN THE SOLID PHASE.

It sometimes occurs in field work that the solutions obtained hold in suspension calcium or magnesium carbonate in the solid phase in a more or less finely divided condition or as a constituent of a clay. Difficulty has been experienced in the use of the method under such conditions; therefore considerable attention has been given to it in the laboratory, both with soils actually found in the field and with artificially prepared mixtures. Many attempts have been made to get around the difficulty. It was hoped that by making the titrations very rapidly approximate determinations could be made; but very unsatisfactory results were obtained, for the rates of solution of both calcium and magnesium carbonate were found to be entirely too high to permit of a satisfactory determination of the end point of a titration with either methyl orange or Congo red as the indicator. It is essential, unfortunately, that the carbonates in the solid phase be removed before making the titrations. Filtration or standing and settling of the suspended matter are serious drawbacks to the use of the method in the field. Attempts are being made to get around the

difficulty, but we are not prepared at the present time to report our work in this direction.¹

PRECAUTIONS IN THE USE OF DISTILLED WATER.

It seems worth while in this connection to call attention to the fact that if a pipette be used for drawing off the portions of the solution for titration, on no account should the contents be blown out by the mouth, for the relative proportion of normal carbonate to hydrogen carbonate may well be disturbed thereby. The distilled water used should have been boiled for some time, and the wash bottle containing it should be fitted with a blow bulb to avoid the necessity of blowing out the contents with the mouth.

ANOMALOUS BEHAVIOR OF CONGO RED.

It has been pointed out by Cohen² that solutions of Congo red do to some extent change color when a stream of carbon dioxide is passed through the solution. This would seem to show that Congo red is an acid weaker than carbonic acid and its use as an indicator in the presence of bicarbonates would be prohibited. This statement of Cohen was confirmed by some experiments made in this laboratory, so far as solutions in pure water are concerned; but when the solutions contained also some salt (such as sodium sulphate or sodium chloride) no effect whatever could be observed when carbon dioxide was passed in.

No explanation is apparent to account for this seemingly anomalous behavior. Experience has amply demonstrated that under the conditions involved in a titration for the estimation of bicarbonates no apparent effect on the Congo red is to be noticed from the carbonic acid dissolved in the solution, either before the titration or as it proceeds.

SUMMARY.

The following conclusions may be drawn from the facts presented:

1. Congo red is a satisfactory indicator for bicarbonates when used in the manner described.
2. Congo red does not interfere with a subsequent titration for chlorides unless present in unusually large amounts.
3. For some eyes and under certain conditions Congo red is to be preferred to methyl orange; for those who can use it, however, methyl orange seems to be the more delicate indicator.
4. It is essential to the satisfactory use of the method that during the titration the solution should not be in contact with carbonates, bicarbonates, or metallic hydroxides in the solid phase.

¹A description of a very efficient filter pump for laboratory or field use will shortly be published by Mr. Briggs.

²Indicators and Test Papers, p. 57 (1899).

